THE HYDROFORMYLATION OF OLEFINS USING
SUPPORTED FILM CATALYSTS

By

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For my family because their love and support are never ending.

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Abstract of Dissertation Presented to the Graduate School
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THE HYDROFORMYLATION OF OLEFINS USING
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The conversion of homogeneous to heterogenous catalytic systems is an
intriguing and a formidable endeavor. Novel approaches to the hybridization of
heterogenous and homogeneous catalysts are described and their effectiveness is
illustrated with the hydroformylation of gaseous and liquid olefins to their
corresponding aldehydes. Supported film catalysts (SFC) utilize a non-volatile film
consisting of a soluble catalytically active complex supported on silica gel. The use
of polymers and other non-volatile films as reaction mediums for SFC's has not been
well established. We have chosen rhodium (I) aryl phosphine complexes in the
presence of excess phosphine for our catalyst due their acute sensitivity to the
reaction environment towards hydroformylation. Supported film catalysts have been
used to hydroformylate propylene, 1-butene and 1,3 butadiene in a gas flow reactor.

The hydroformylation of propylene shows selectivities greater than 99% to n-butyraldehyde under mild conditions.

Extending SFC's to liquid substrates, such as 1-hexene, presents the added problem of leaching the active catalyst and/or film phase into the solvent during catalysis. We have developed a system which uses hydrophilic polymers (ie. polyethylene glycol) and catalysts supported on silica gel to inhibit leaching during the reaction. The rhodium complex $HRh(CO)(TPPTS)_3$ (TPPTS = triphenylphosphine trisulfonate sodium salt) has been selected as the catalyst due to its hydrophilic nature. Comparisons of the SFC's to supported aqueous phase catalysts (SAPC) and to biphasic aqueous systems are made. Unusually high activities and moderate selectivities are observed at temperatures ranging between 75°C and 125°C and pressures of 50 psig syn gas.

CHAPTER 1
INTRODUCTION

The focus of this dissertation is the development of a new class of supported liquid phase catalysts (SLPC). Suppored liquid phase catalysts are heterogeneous catalysts in which a liquid film containing a soluble catalyst coats a support (generally inorganic oxides). To date the majority of the liquid phases have consisted of high boiling liquids. These liquids have some volatility and may evaporate from the support with time. The catalysts presented herein utilize non-volatile films such as polymers and molten salts as replacements for the high boiling liquids and will be given the general term supported Film catalysts (SFC).

The hydroformylation of olefins with rhodium catalysts has been chosen as the test system for the new catalysts. There are several reasons for this selection. 1. Rhodium catalysts are the most active catalyst for hydroformylation. This high activity makes for easy analysis and evaluation of the catalysts. 2. The environment of the rhodium catalyst influences both the activity and selectivity of the catalyst. 3. Catalytic conversion of olefins to aldehydes is a vital chemical industry. It is the largest commercial homogeneous catalytic process.

This study is divided into two areas. The first concerns the hydroformylation of gaseous substrates such as propylene. The second studies the hydroformylation

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of liquid substrates (e.g. 1-hexene) with a subclass of SFC's, supported hydrophilic

film catalysts (SHFC).

CHAPTER 2
BACKGROUND AND MECHANISMS OF THE RHODIUM CATALYZED HYDROFORMYLATION OF OLEFINS

Introduction

Background

Hydroformylation or the "oxo" process is the reaction of hydrogen and carbon monoxide with olefins in the presence of a catalyst to form aldehydes. Although the reaction is energetically favorable (-28 Kcal/mol) it does not occur to a measurable extent in the absence of a catalyst.[1] Generally, with low molecular weight olefins two major products are formed, the linear and branched aldehydes; economically the linear aldehyde is preferred. The reaction is depicted in Figure 2-1. Side reactions such as isomerization and hydrogenation also occur. These will be discussed in greater detail later.

Hydroformylation was discovered by Otto Roelen in 1938 in Germany while studying the activity of ethylene under Fischer-Tropsch reaction conditions.[2,3] Since that time, this process has found its place in the petrochemicals industry. Approximately 10 billion pounds of products are made annually via the hydroformylation process, making it the largest homogeneous catalytic process.[4,5] The largest classification of substrates for this process are gaseous olefins (C_2-C_4). Table 2-1 shows some commercial catalytic systems.[6]

$$RCH{=}CH_2 \xrightarrow[\text{Catalyst}]{H_2/CO}$$

$$\overset{\displaystyle O}{\underset{}{RCH_2CH_2\overset{\|}{C}H}} \quad \text{Linear}$$

$$+$$

$$\underset{CH_3}{RCH_2\overset{|}{C}H\overset{\overset{\displaystyle O}{\|}}{C}H} \quad \text{Branched}$$
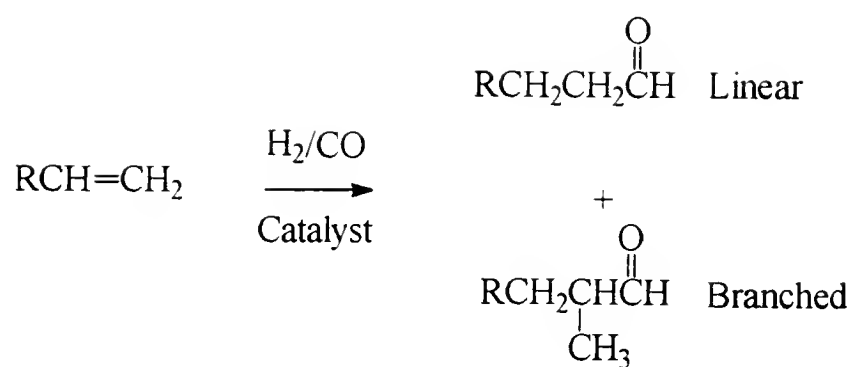
Figure 2-1. Hydroformylation reaction of olefins to aldehydes.

Table 2-1. Commercial Hydroformylation Systems.[a]

Catalyst	Temperature (°C)	Pressure (psig)	Selectivity (%)	n/i Ratio	Metal/Olefin (%)	Olefins
$Co_2(CO)_8$	140-180	3500-5000	80	4/1	0.1-1.0	C_2-C_{12}
$Co_2(CO)_6(PBu)_2$	160-200	735-1470	80	8/1	0.5-1.0	C_2-C_{12}
$HRh(CO)(PPh_3)_3$	80-120	220-370	96	10/1	10^{-2}-10^{-3}	C_2-C_4
$HRh(CO)(TPPTS)_3$	80-130	590-735	99	19/1	0.2	C_2-C_4

[a] Adapted from reference 6.

It should be noted that aldehydes themselves are not very useful but are precursors to other more economically attractive chemicals. Aldehydes can be hydrogenated to alcohols or oxidized to carboxylic acids. These in turn can be further processed to plasticizers, metal working fluids, alkyd resins, specialty greases and surfactants.[7]

$$RCH_2CH_2CH_2CHO \xrightarrow[\text{Catalyst}]{H_2} RCH_2CH_2CH_2CHOH$$

$$RCH_2CH_2CH_2CHO \xrightarrow[\text{Catalyst}]{O_2} RCH_2CH_2CH_2COOH$$
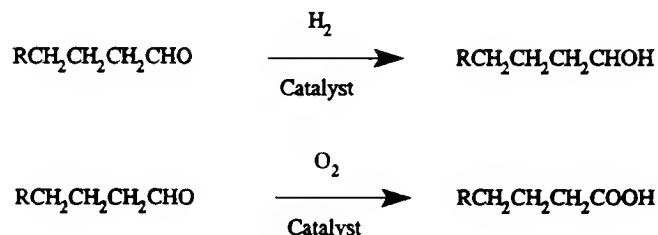
Several transition metal carbonyls are known hydroformylation catalysts. In order of decreasing activities they are Rh, Co, Ru, Mn, Fe, Cr, Mo, W, Ni, Pt and Cu.[8] Rhodium and cobalt carbonyls are the most commonly studied and are the only catalysts active enough for use as commercial catalysts. Rhodium catalysts are approximately 3500 times more active than cobalt. In addition, the rhodium catalysts modified with phosphine ligands are more selective than cobalt catalysts. The principal disadvantage of rhodium catalysts is cost, currently $RhCl_3 \cdot 3H_2O$ is \$145/gr.[9]

Table 2-2 lists several substrates that can be hydroformylated with rhodium complexes and their relative rates of reaction. Linear olefins such as 1-hexene and 1-octene are more readily hydroformylated than the branched or internal alkenes, such as 2-methyl 1-pentene and 2-hexene.[1]

Table 2-2.   Hydroformylation   Rates   of   Various   Olefins   Using
$HRh(CO)(PPh_3)_3$ as the Catalyst at 25°C.

Substrate	Turnover Rate (TON/hr)
Allyl Alcohol	4.50
Styrene	2.80
1,5 Hexadiene	2.70
1-Pentene	2.40
Allyl cyanide	2.40
Ethylene	2.40
1-Hexene	2.30
1-Dodecene	2.00
Cyclooctene	0.17
2-Pentene	0.10
2-Methyl-1-pentene	0.04
Cyclohexene	0.03
1,3-Butadiene	0.00
Tetrafluoroethylene	0.00

Phosphine Modified Rhodium Catalysts

Rhodium is by far the most active metal for the hydroformylation of olefins. Reaction rates and product distributions depend on a number of reaction variables. These include the substrate and ligand type, the concentrations of the reactants (hydrogen, carbon monoxide and olefin), the concentration of the catalyst and ligand, and the reaction temperature. The difficulties with these catalysts are the undesirable isomerization of olefins and the instability of the catalysts. The addition of phosphine ligands to these systems not only improves the selectivity and activity of the catalysts but also increases catalyst lifetimes and reduces the amount of isomerization in the system.,[10,11,12]

Effects of equilibrium positions and mechanisms

It has been shown that in the presence of hydrogen, carbon monoxide and excess phosphine, most any rhodium(I) complex is converted to the form $HRh(CO)_x P_y$ (P=phosphine).[13] Depending on the concentration of the reactants, several carbonyl/phosphine species exist in solution (see Figure 2-2).[14,15,16] These intermediates are thought to be the active catalytic species for hydroformylation. Both the selectivity and rate of reaction are influenced by the position of the equilibria that are established with reactant variation.

$$HRh(CO)_2(PPh_3)$$
$$\underline{D}$$

$$-PPh_3 \upharpoonleft\downharpoonright +PPh_3$$

$$HRh(CO)(PPh_3)_3 \quad \overset{CO}{\underset{PPh_3}{\rightleftharpoons}} \quad HRh(CO)_2(PPh_3)_2 \quad \overset{CO}{\underset{PPh_3}{\rightleftharpoons}} \quad [HRh(CO)_3(PPh_3)]$$
$$\underline{B} \qquad\qquad\qquad \underline{A} \qquad\qquad\qquad \underline{C}$$

$$-PPh_3 \upharpoonleft\downharpoonright +PPh_3 \qquad\qquad -CO \upharpoonleft\downharpoonright +CO$$

$$HRh(CO)(PPh_3)_2 \qquad\qquad HRh(CO)(PPh_3)_2$$
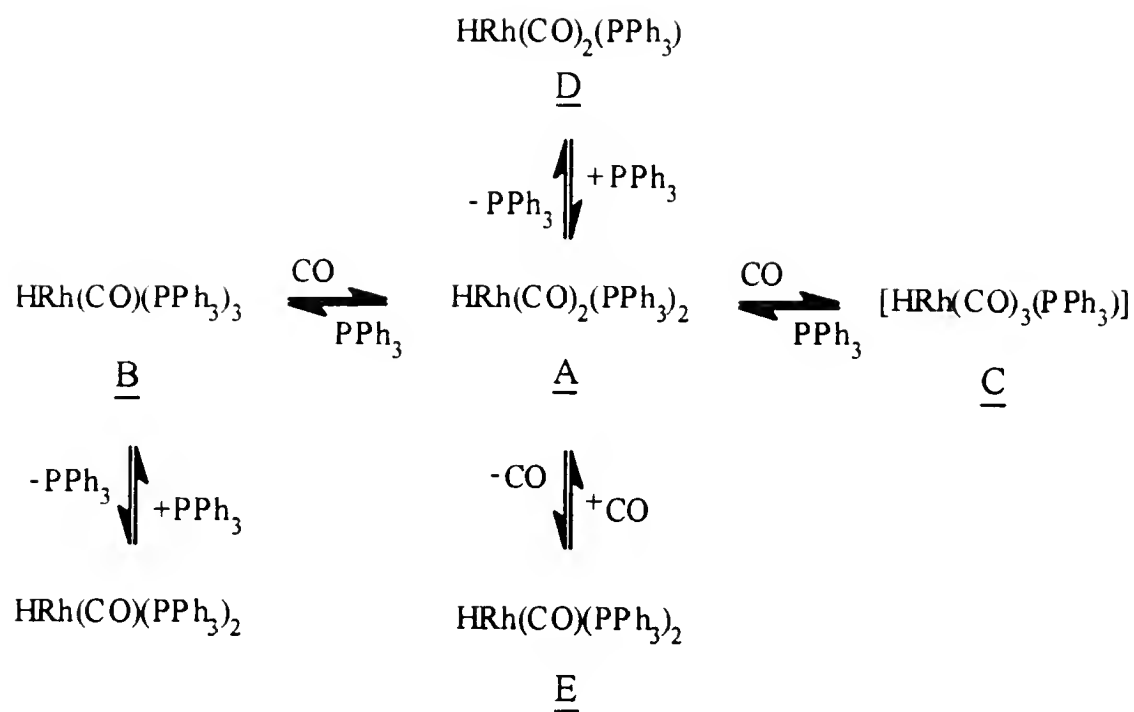$$\underline{E}$$

Figure 2-2. Equilibrium species of hydrido rhodium carbonyl phosphine complexes.

The predominant species for hydroformylation under standard conditions $(H_2/CO$ of 1:1 and no excess phosphine) is the 18 electron species $HRh(CO)_2(P)_2$ ($\underline{A}$). From this intermediate either the associative or dissociative mechanism can be followed as proposed by Wilkinson (see Figure 2-3).[11,12,13,15,17,18,19,20,21,22,23]

The associative route starts when $HRh(CO)(PR_3)(L)_2$ (L = PR_3 or CO) dissociates a phosphine to form the 16 electron species $HRh(L)_3$ ($\underline{1}$). This complex then can add CO rapidly to form the active catalytic species, $HRh(CO)(L)_3$ ($\underline{2}$), which corresponds to $\underline{A}$, $\underline{B}$, and $\underline{C}$ in Figure 2-2. Olefin can then bind to the rhodium complex to form $HRh(CO)(L)_3(RCH=CH_2)$ ($\underline{3}$) and then rearranges rapidly to the 18 electron species $Rh(CO)(L)_3(CH_2CH_2R)$ ($\underline{4}$). It is this rearrangement where the selectivity takes place. Anti-Markovnikov addition leads to the linear alkyl species and hence a linear product, while Markovnikov to a branched metal alkyl which produces branched aldehydes (see Figure 2-4). Bulky phosphines promote anti-Markovnikov addition. From here CO insertion/alkyl migration yields the acyl complex $\underline{5}$. Formation of linear products is favored by the associative route. This is attributed to the more sterically hindered olefin coordination.

Dissociative mechanism occurs when another phosphine dissociates from $\underline{2}$ to give $HRh(CO)(L)_2$ ($\underline{7}$) which then binds the olefin to form $\underline{8}$ and rearrangement occurs to form $\underline{9}$. Due to the loss of phosphine there is a lack of steric influence and Markovnikov addition occurs more readily than in the associative path, hence favoring branched products. Addition of the phosphine and CO insertion/alkyl migration gives $\underline{4}$, the common intermediate in both pathways.
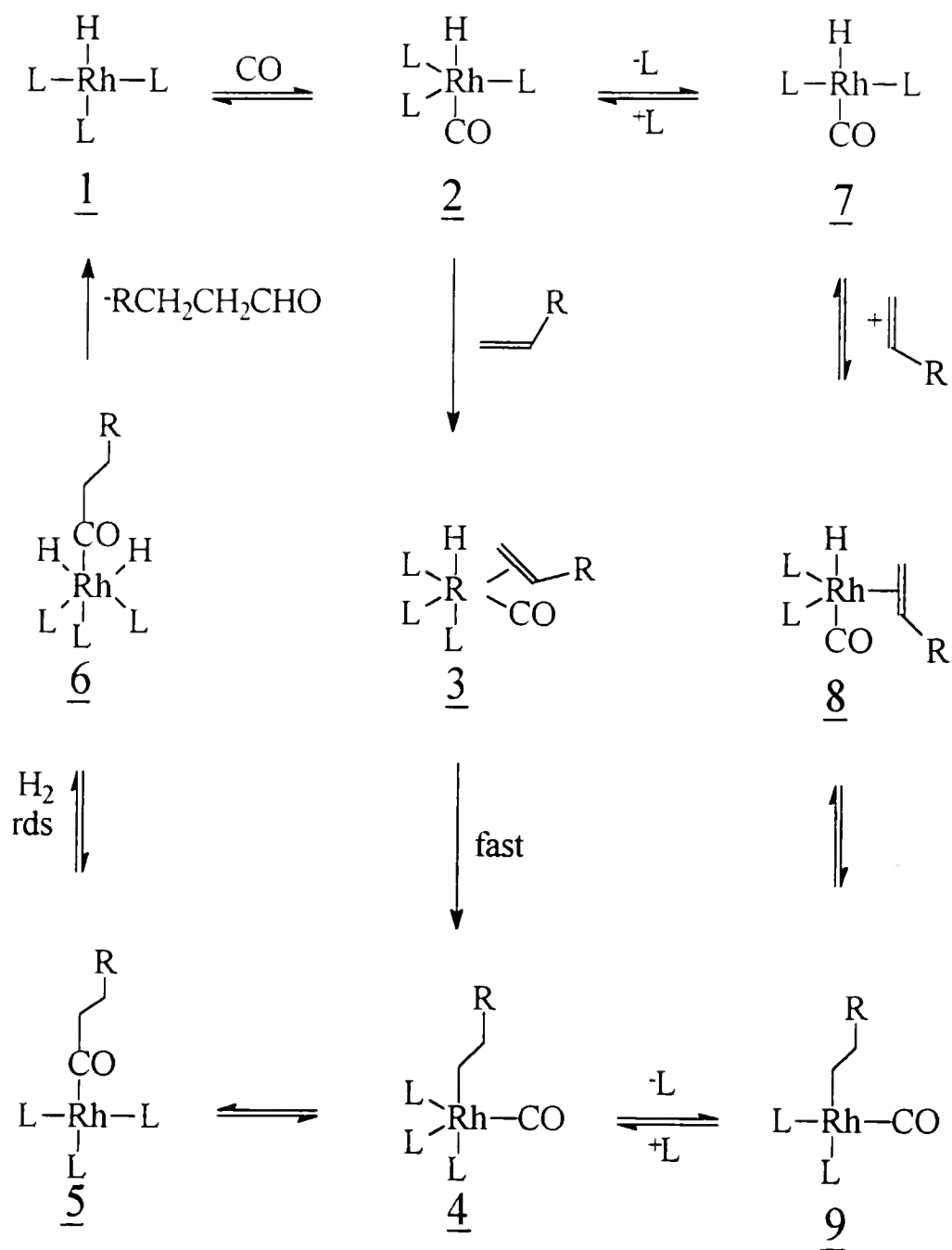
Figure 2-3. Mechanisms for the hydroformylation of olefins.

Anti-Markovnikov Addition

Markovnikov Addition
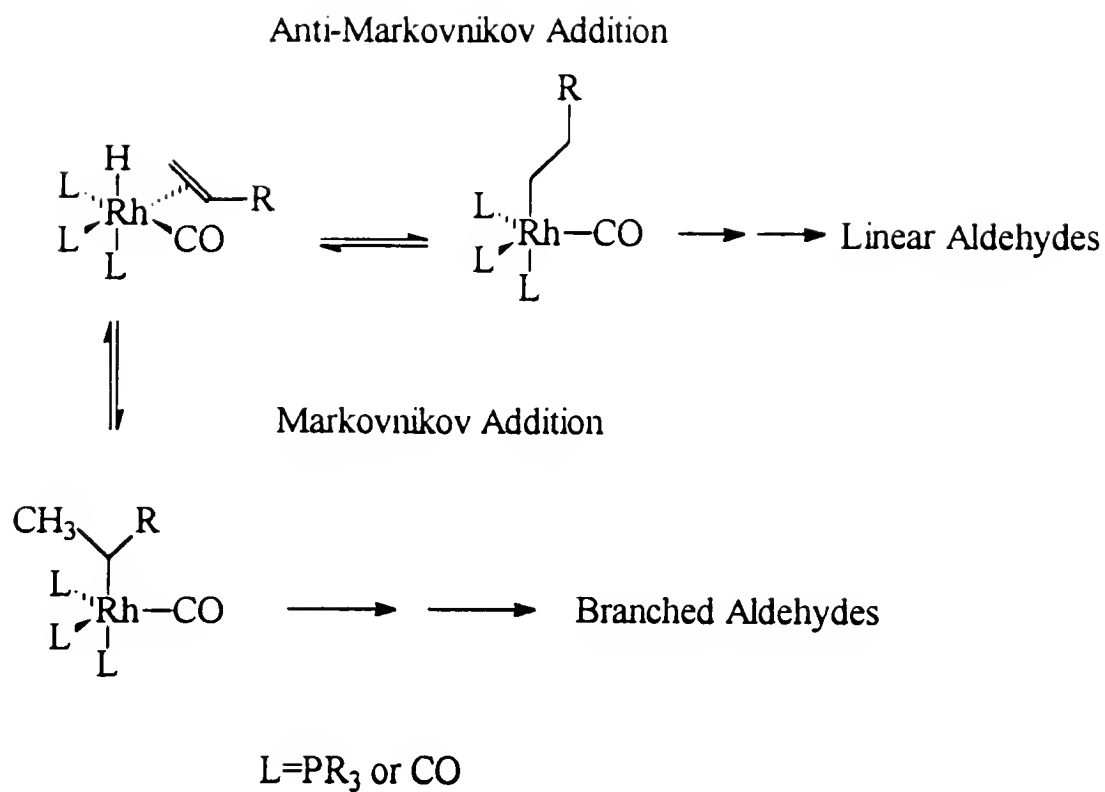
Branched Aldehydes

L=PR$_3$ or CO

Figure 2-4. Anti-Markovnikov and Markovnikov addition
to the rhodium catalyst.

In both mechanisms oxidative addition of H_2 to the acyl complex gives the six coordinate intermediate <u>6</u>. This is the rate determining step. Alternatively CO could add to the acyl complex to give $Rh(L)_3(CO)$-acyl which is catalytically inactive. Reductive elimination then yields an aldehyde and the square planar complex $HRh(L)_3$ (<u>1</u>).

Phosphine concentration effects the rate of reaction as well as the n/b ratio. Figure 2-5 shows the effect of the change in phosphine using a 1-hexene feed. As the concentration of phosphine increases the rate initially increases until the phosphine to rhodium ratio (P/Rh) is in the 20:1 - 50:1 and then decreases. The n/b ratio increases with the P/Rh ratio.[7] If the concentration of phosphine is high, the resultant rhodium catalyst has a high degree of substitution by phosphines and the active catalyst exists as the 18 electron species $HRh(CO)(P)_3$ (<u>B</u>), refer back to Figure 2-2. This follows the associative pathway which allows a high selectivity towards linear aldehydes but slow rates of reaction. In the case of low phosphine concentrations a phosphine dissociates from <u>A</u> to form the 16 electron species $HRh(CO)_2(P)$ (<u>D</u>). Hence the dissociative route predominates. The result is an increase in the reaction rate but a loss in selectivity.[12]

At low carbon monoxide concentrations <u>A</u> can dissociate a carbonyl to form the 16 electron complex, $HRh(CO)(P)_2$ (<u>E</u>). This intermediate allows for high rates of reactions but also the less selective dissociative mechanism to predominate. At high carbon monoxide concentrations the reaction is inhibited.
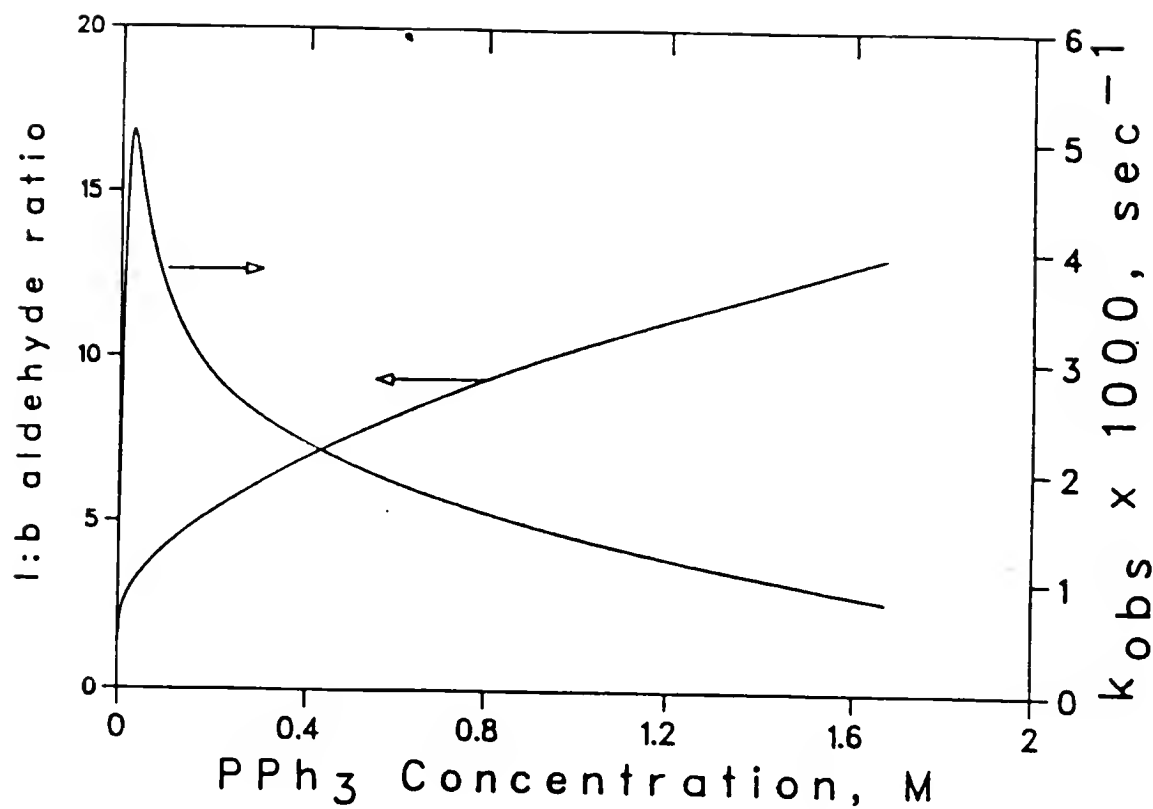
Figure 2-5. Effects of phosphine concentration on the activity
and product distribution of rhodium catalyzed
hydroformylation of 1-hexene.

The changes in reaction rates and product distribution can be explained by the steric influence of the ligands. Phosphine ligands are more sterically hindering than carbon monoxide. Upon coordination of a phosphine ligand there is relatively less area about the metal for olefin coordination. This causes the olefin to favor anti-Markovnikov addition to the metal, resulting in a higher selectivity towards linear aldehydes.[16]

An undesirable side reaction of hydroformylation is the isomerization of α-olefins to internal olefins (see Figure 2-6). The undesirability is derived from the fact that internal olefins are much less reactive than their alpha counterparts (see Table 2-2), and the resultant aldehydes usually are of no economic importance. Isomerization is thought to come about by olefin coordination to $HRh(CO)(L)_2$ (1) prior to CO addition (see Figure 2-3). Isomerization can be repressed by the addition of excess phosphine ligand.[24,25]

In addition to the degree of substitution, the size and basicity of the ligand effects catalyst performance (see Table 2-3). Bulkier ligands yield a more selective catalyst, and as the basicity of the ligand decreases the activity and selectivity increases.[17] In the same vein less bulky phosphines are more susceptible to substitution by CO resulting in decreased in selectivity. As L is substituted by CO poor selectivity is realized.

In addition to ligand effects many variables control the activity and product distribution of hydroformylation catalysts. These include the concentration of the substrate, hydrogen, carbon monoxide, rhodium, and ligand as well as temperature,
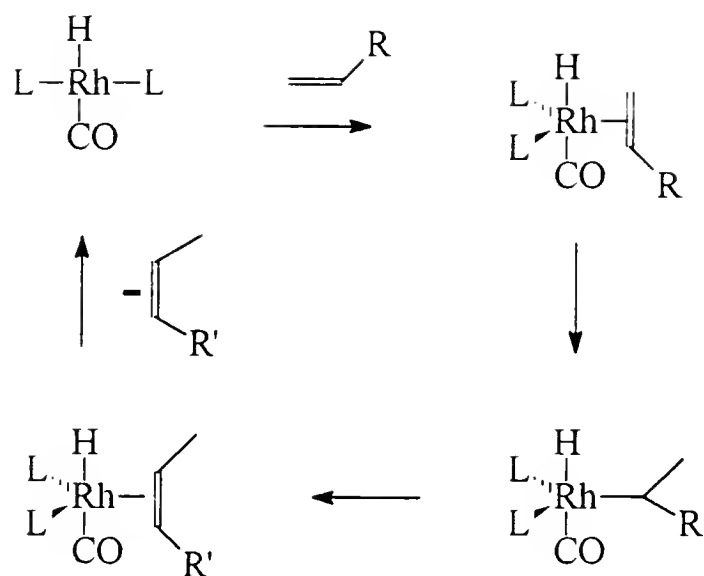
Figure 2-6. Mechanism for the isomerization of olefins.

Table 2-3. Dependence of Product Distribution on Phosphine Ligands in the Hydroformylation of 1-Octene.

Ligand	Percent Linear Aldehyde	Reaction Time (min)	Cone Angle (°)	$v(cm^{-1})^b$
$P(OC_6H_4p\text{-}Cl)_3$	93	55	128	33.2
$P(OPh)_3$	86	50	128	29.2
$P(OC_6H_44pPh)_3$	85	70	128	28.9
$P(OC_6H_4pOMe)_3$	83	270	128	28.0
PPh_3	82	35	145	12.8
$P(OBu)_3$	81	60	107	20.2
$P(OC_6H_4Ph)_3$	78	52	141	28.0
PBu_3	71	225	132	4.2
$P(OC_6H_4o\text{-}Ph)_3$	52	95	132	28.9
$P(O\text{-}2,6\text{-}Me_2C_6H_3)_3$	47	80	190	27.1

[a] 112 g 1-octene, 10 g 5% Rh/C, and 0.05 mol L (L:Rh = 10:1) with 80-100 psig of 1:1 H_2/CO at 90°C. Adapted from reference 1.
[b] $v = m\text{-}2056.1$ cm^{-1}.

pressure and solvent polarity. Table 2-4 shows intrinsically how the increase of a variable influences the reaction rate and product distribution of rhodium catalysts. Solvent polarity and basicity contribute to the reaction selectivity. As a general rule, selectivity increases as solvent polarity and basicity increase.[12]

Table 2-4.   Effects of Reaction Variables on the Rate and Selectivities of Rhodium Hydroformylation Catalysts.[a]

Variables	Rate	n/b Ratio	Isomerization
[H$_2$]	+	+	+
[CO]	-	-	-
[olefin]	+	0	[b]
Increasing Temperature	+	±	+
[Rh]	+	+	[b]
[L]	-	+	-

[a]   Based on the hydroformylation of 1-hexene in benzene using HRh(CO)(TPP) as the rhodium source. + indicates an increase and - a decrease.   Abbreviations: [H$_2$], [CO] [olefin], [Rh] and [L] are the concentration of hydrogen, carbon monoxide, olefin rhodium, and ligand, respectively. Adapted from reference 1.

[b]   Not reported.

CHAPTER 3
HYDROFORMYLATION OF GASEOUS SUBSTRATES

Introduction

Homogeneous hydroformylation of olefins has matured into a finely tuned art. Rhodium catalysts are optimal catalysts for hydroformylation yielding systems which are unusually active and showing selectivities as high as 10:1 to the linear aldehyde. However, the drawbacks of these systems, namely the recovery of valuable rhodium catalysts and the convenient separation of products from the reaction solution, merit study.

Heterogeneous catalysts have been designed to circumvent the shortcomings of homogenous systems. Several methods have been used to immobilize homogenous catalysts. These include 1. chemisorption of the metal complex on a solid support; 2. physical adsorption of a catalytic complex; 3. entrapment of complexes in zeolites; 4. coordination of the metal complex to functionalized polymers or inorganic oxides; and 5. supported liquid phase catalysts. These techniques have yet to produce a commercially viable catalyst for hydroformylation. The lack of success can be attributed to leaching of the metal from the support to the surrounding environment and to the loss in activity and selectivity associated with immobilization of homogenous catalysts. This chapter will concentrate on heterogeneous catalysts as

they pertain to the hydroformylation of gaseous substrates, such as propylene and 1-butene.

Supported Liquid Phase Catalysts (SLPC)

Of all the types of heterogenous catalysts, supported liquid phase catalysts (SLPC) seem to have the most promise in the commercialization of a catalytic process. SLPCs are true hybrids of homogeneous and heterogeneous catalysts in that a support is coated with a catalytic film that consists of a homogeneous catalyst and a high boiling liquid.[26,27] Several applications of supported liquid phase catalysts exist, these include the oxidation of SO_2,[28] dimerization of alkenes,[29] and Wacker oxidation.[30] However, the largest application of SLPC has come in the field of hydroformylation.

A multitude of catalytic supports are known. Some supports (e.g. porous glass and macroreticular polymer resins) are inert, while others (e.g. silica and alumina) possess acid/base properties.[31] These sites may synergistically enhance the activity of the catalyst or may act to anchor the catalyst to the support.[32] The chemical alteration of organic polymers and inorganic oxides creates ligands to coordinate active metal species but they can also change the activity of a catalyst.

The interactions of the metal complexes and/or additives with the support are important.[33] If the support deactivates a complex or competes for the ligands rendering them unavailable for coordination, then that material may be a poor support for SLPC. As previously stated, triphenylphosphine is an important additive

for most rhodium based hydroformylation catalysts. Triphenylphosphine can chemisorb on alumina (see Figure 3-1). In addition, triphenylphosphine can also hydrogen bond to the inorganic oxide surface (see Figure 3-2). These phosphines are bound tightly and are not available for coordination to the rhodium complexes. Rhodium complexes are known to chemisorb to the surface of alumina (see Figure 3-3). In the presence of excess phosphine the chemisorption of the rhodium is eliminated.

SLPC for the hydrformylation of gaseous substrates

Supported liquid phase catalysts are active for the hydroformylation of gaseous alkene substrates and realize long term stability in gas flow reactors.[34] Generally, conditions for reaction range from 80-125°C and 250-1000 psig. Table 3-1 shows the activity and selectivity of some selected catalysts. Activities varied with the change in support, liquid phase and transition metal complex. Most systems studied used phosphine modified rhodium catalysts and high boiling liquids as the catalytic liquid phase. Catalysts which possess a liquid phase have been shown to be more active than their surface bound counterparts consisting of the same rhodium sources and supports.[35] It has been observed that in these systems the reaction rate is diffusionally retarded.

A crucial requirement for an efficient catalyst in a gas flow reactor is that reactants and products must be gases at reaction temperatures. This minimizes condensation of the substrates and/or products in the pores of the support.
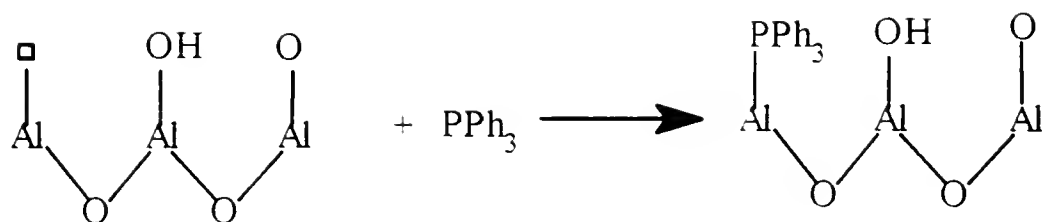
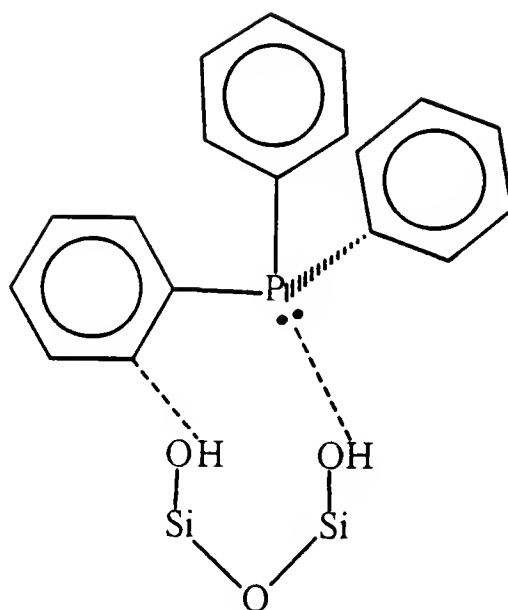Figure 3-1. Adsorption of triphenylphosphine on alumina.
□ - anion vacancy
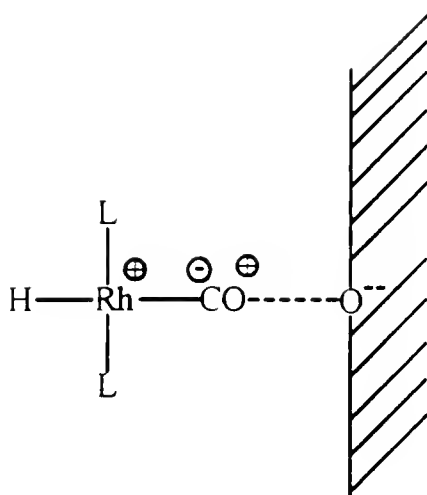
Figure 3-2. Adsorption of triphenylphosphine on silica.

Figure 3-3. Adsorption of rhodium phosphine complex on an oxide surface. L= triphenylphosphine

Table 3-1. Hydroformylation of Propylene with SLPC.

Support	Liquid Phase	Metal Complex	T(°C)	P (psig)	Activity	n:i	Ref.
Alumina	none	$(PPh_3)_2Rh(CO)Cl$	90	705	36	1.9	45
carbon	none	$(PPh_3)_2Rh(CO)Cl$	90	705	46	1.25	45
alumina	1	$(PPh_3)_2Rh(CO)Cl$	90	705	41	2.7	35
alumina	2	$(PPh_3)_2Rh(CO)Cl$	90	705	23	1.9	35
carbon	2	$(AsPPh_3)_3Rh(CO)Cl$	90	705	32	1.9	35
diatomaceous earth	2	$Co_2(CO)_6(PBu_3)_2$	90	705	9	2	35
alumina	none	$(PPh_3)_2Rh(CO)Cl$	90	705	36	1.9	35
carbon	none	$(PPh_3)_2Rh(CO)Cl$	90	705	46	1.2	35
c alumina	none	$Rh(\pi\text{-allyl})(CO)(PPh_3)_2$	90	1.57	0.004	2	35
c alumina	3	$Rh(\pi\text{-allyl})(CO)(PPh_3)_2$	90	1.57	0.025	9.3	34
alumina	4	$HRh(CO)(PPh_3)_3{}^a$	90	1.57	0.105	3.1	34
carbosil[b]	none	Rh	125	6.87	0.077	1.1	34
silica gel	5	$HRh(CO)(PPh_3)_3$	136	3.48	0.66	2.0	34

1. diphenylether; 2. diphenyl 2-ethylhexylphosphate; 3. triphenylphosphate; 4. 2-ethylhexylphthalate; 5. butylbenzylphthalate.

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[a] P/Rh ratio of 56.

[b] Functialized with $(C_2H_5O)_3Si(CH_2)_2-P(C_6H_5)_2$

A catalyst with a liquid phase of butylbenzylphthalate and $(PPh_3)_2Rh(CO)Cl$ and excess phosphine on an alumina support exhibits an optimal activity at a liquid loading of 0.5 cm³ per gram of catalyst.

Aldehydes, the products of hydroformylation are soluble in many of the liquid phases. Three possible scenarios may develop: 1. As the reaction proceeds, the amount of alkanals condensed in the pores fill the pores so that the degree of pore filling, δ, is greater than one, this leads to leaching of the transition metal catalyst.[36] 2. The amount of rhodium complex adsorbed to the surface is influenced. 3. The amount of alkanals in the liquid phase influences the equilibria between various dissolved rhodium complexes.

A study of SLPCs which utilize molten triphenylphosphine as the liquid phase showed that condensed aldehydes are discernibly soluble in the liquid phase of the catalyst, but the solubility of hydrogen and carbon monoxide in this medium is not appreciably effected. However, the solubility of the alkene is strongly influenced.[35] A SLPC in which aldehyde was added to the film led to a lowering of the linear to branched ratio from 20 to 15 but an increase in activity by 10%.[37]

Degree of pore filling and its relation to activity and selectivity

The degree of pore filling, δ, greatly effects the activity of most SLPCs for the hydroformylation of olefins.[38,39] In an ideal system, the liquid phase covers the entire surface uniformly then preferentially fills the smallest pores (see Figure 3-4).[40] Due to the complexity and non-uniform nature of the pore structure of many
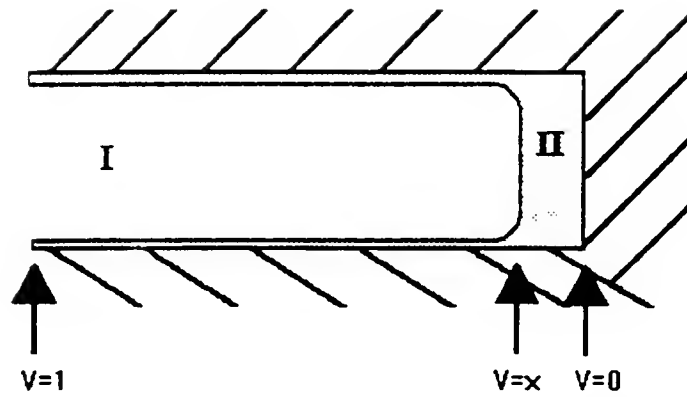
Figure 3-4.   Diagram of an ideal liquid filled macropore. The fraction of total pore length that is occupied by a liquid plug is denoted by x. Adapted from reference 42.

supports the description of SLPCs can only be done with statistical parameters. Rony et al.[41] utilized these parameters to describe the optimal loading for an alumina support with a butylbenzylphthalate liquid phase, they found that the optimal value of δ was 0.5 cm^3 liquid/cm^3 pore (see Figure 3-5). The activity decreases as the pores become filled. It has been claimed that it is rarely beneficial to pore fill over this value. This is due to the long liquid diffusion paths as δ approaches 1.

Generally for a given system, the activity reaches a maximum and then decreases with increasing δ. Most of the catalysis occurs at the gas/liquid interface, and it follows that the increase in activity is due to the increase of the gas/liquid interface. Low or no pore filling leads to catalysts which bound to the support. On the other hand, SLPCs with a large δ contain liquid plugs or pools of solution in the pores. In these areas the majority of the rhodium catalyst exists in the bulk solution, which possesses a high concentration of phosphine and a low concentration of carbon monoxide and substrate. This gives rise to highly substituted rhodium phosphine species which favors selectivity to linear products. However, due to the decrease in the gas/liquid interface, the activity of these systems are greatly reduced.

Other Heterogeneous Catalysts

Hydroformylation in polymer matrices

The deposition of rhodium catalysts in thin polymer films provide marginally active hydroformylation catalysts for ethylene and propylene. A film of cellulose acetate and HRh(CO)(PPh$_3$)$_3$ gives an activity of 0.41 TON/min under atmospheric
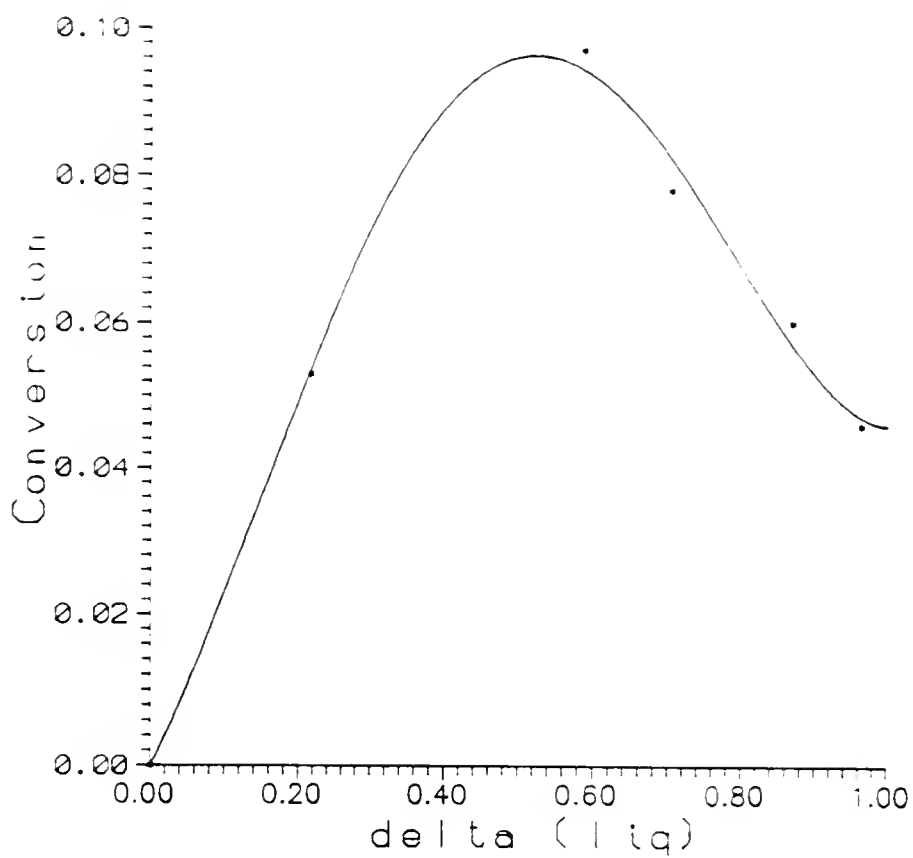
Figure 3-5.   Conversion curves for the hydroformylation of propylene as a function of liquid loading. The liquid phase is butylbenzylphthalate. Adapted from refence 42.

pressures and 80°C.[42] Active catalysts for hydroformylation also are formed in polystyrene and polybutylmethacrylate films.

Chemisorbed catalysts

Silica supports. A strong affinity between silica and $HRh(CO)(PPh_3)_3$ exists and is evidenced by the decolorization of a $HRh(CO)(PPh_3)_3$ benzene solution in the presence of silica.[43] Phosphine modified rhodium complexes impregnated on alumina or carbon have activities >30% and n/b ratios of 2. Good long term stability over a 300 hour period are seen for these catalysts.[44]
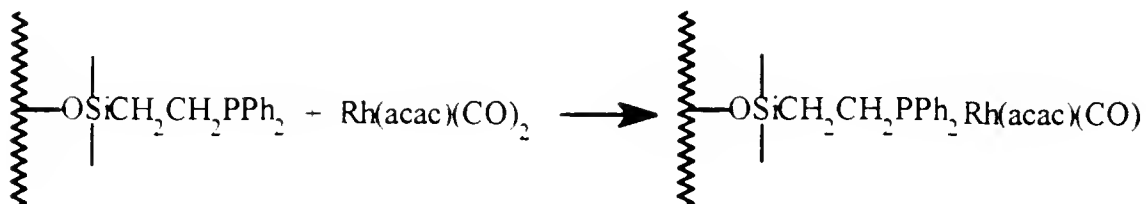
Functionalized supports

Inorganic oxide supports. Coordinating homogenous catalytic complexes to functionalized organic polymers or inorganic oxides with ligand derivatives is a common method of heteroginizing homogenous catalysts. Functionalized silica with phosphorous, nitrogen and oxygen donor ligands have been prepared.[45,46] In the case of hydroformylation, rhodium is commonly used as a catalyst. Figure 3-6 shows the preparation of an immobilized rhodium catalyst on a functionalized silica support.

Functionalized polymers. Polystyrene and divinylbenzene based polymers are by far the most common choice for functionalized supports.[47] This is because the aromatic side chains are easily modified to contain phosphine side chains, which are good ligands for rhodium hydroformylation catalysts (see Figure 3-7). Copolymers have been designed by cross-linking to create supports which are porous, insoluble and swellable.[48]
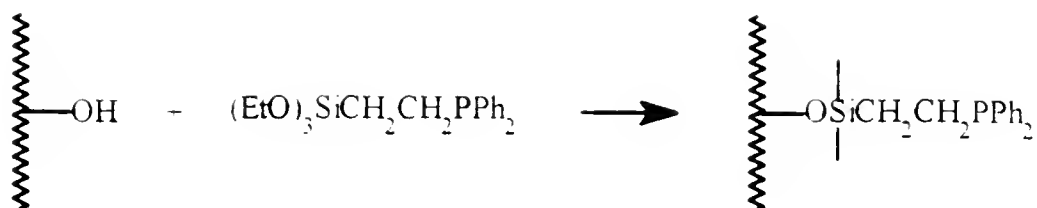
Figure 3-6.   Preparation of an immobilized catalyst by coordination
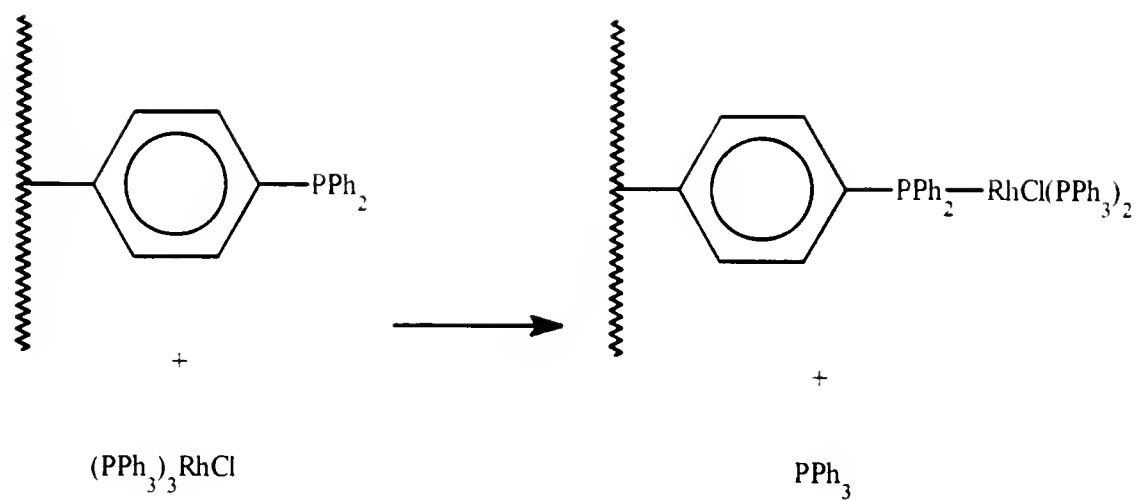to a functionalized silica support.

Figure 3-7. Preparation of an immobilized catalyst by coordination to a functionalized polymer.

The rigidity of the polymer also plays an important role in activity.[49] If the polymer chain has low flexibility the access of reactants to the metal center decreases, hence a decrease in activity.[50,51] On the other hand, if the chains are too mobile, deactivation of the rhodium may occur by the formation of rhodium clusters.[52,53]

Due to preferred conformations within the polymer some of the phosphines may be unavailable for coordination to the metal center. If the number of coordinated ligands to a rhodium center is considerably lower than in homogeneous systems depends, it follows that the selectivity for the polymer system is lower.[52]

Zeolites

Rhodium catalysts have been incorporated into zeolites and used in the vapor phase hydroformylation of olefins.[54,55] The hydroformylation of substrates shows activity towards ethylene, propylene and 1-butene at 150°C and at a n/b ratio of 2:1.[56] These catalyst have demonstrated stability for up to one month.

Experimental

Chemicals

The following were used without any further purification: $RhCl_3 \cdot 3H_2O$ (Strem

Chemical Inc.); triphenylphosphine (Aldrich); potassium hydroxide (Fisher); absolute

ethyl alcohol (Florida Distilleries); hexanes (Fisher); chloroform (Fisher); polybutyl-

methacrcrylate (Aldrich); silicon gum rubber (Varian); polybutadiene (Aldrich);

Aliquat 336 (Aldrich); tetrabutylphosphonium chloride (Aldrich); formaldehyde

(Aldrich); propylene carbonate (Fisher); 1-octanol (Fisher); silica gel (Davison, pore

volume 1.1 mL/g); hydrogen (Matheson); carbon monoxide (Matheson); propylene

(Matheson); 1-butene (Matheson); 1,3 butadiene (Matheson).

Synthesis of Reagents

Preparation of Hydridocarbonyltris(triphenylphosphine)rhodium, $HRh(CO)(PPh_3)_3$

Synthesis of $HRh(CO)(PPh_3)_3$ was carried out as reported.[57] Under an

atmosphere of nitrogen, triphenylphosphine (2.64g, 10 mmol) was added to refluxing

ethyl alcohol (100mL, absolute). To this $RhCl_3 \cdot 3H_2O$ (0.26g, 1.0 mmol) in hot ethyl

alcohol (20mL) was added. After a 15 second delay, formaldehyde (10mL, 37% in

water) followed immediately by potassium hydroxide (0.8g) in hot ethyl alcohol

(20mL) were added. It should be noted that the addition of the reactants in the

indicated order is critical in this synthesis. Upon addition of potassium hydroxide the

solution turns yellow and the formation of a precipitate is evident. The yellow

mixture was allowed to reflux an addition 10 minutes then cool with stirring to room temperature. The yellow solid was filtered, washed with ethanol (2x10mL), followed by H_2O (2x10mL), then again with ethanol (2x10mL) and finally by hexanes (10ml). The yellow solid is dried under vacuum at 40°C for 18 hours. Infra red bands v_{CO}=1919 (lit. 1918), v_{Rh-H}=2037 (lit. 2041).

Preparation of Supported Film Catalysts

The following is a description of the preparation of a typical catalyst.

A solution of chloroform (25mL) and polybutyl-methacrcrylate (0.06g) was added to a solid mixture containing $HRh[P(C_6H_5)]_3(CO)$ (0.10g), 0.262gm of triphenylphosphine (0.262g) and silica gel (0.60g). After 2 minutes of stirring the solvent was removed under reduced pressure at room temperature. The yellow powder was dried under vacuum overnight with the temperature not to exceed 45°C.

A 0.50 g sample of this product was placed in a stainless steel column of a gas flow reactor (Figure 3-8) which was placed in an preheated constant temperature oil bath at the specified reaction temperature. A premixed gas of H_2/CO/propylene, also at specified pressures and flow rates was fed through the reactor. Analysis was performed by an on-line gas chromatograph. Table 3-2 is a compilation of the experiments presented in the Results and Discussion section.
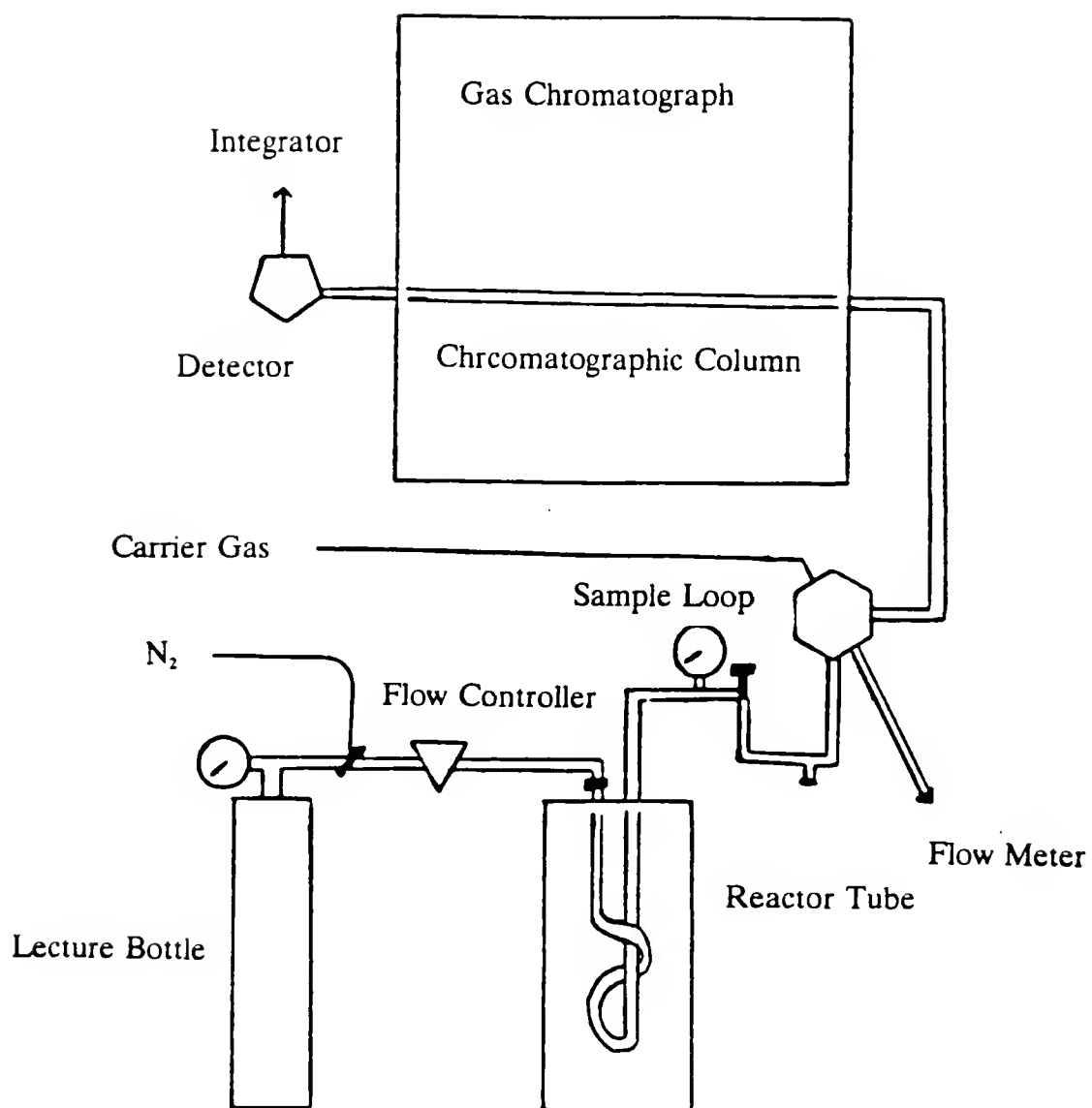
Figure 3-8. Schematic for a gas flow reactor with an on-line gas chromatograph.

Table 3-2. Compilation of the Data for the Hydroformylation of Propylene with Support Catalytic Film Catalysts.

Film	[Rh]	delta	P/Rh	Temperature (Celcius)	Pressure (psig)	Gas Mixture (H2/CO/C3H6)	Flow Rate	Activity	n/b Ratio
PBMA	0.13	0.25	0	100	20	1/1/0.1	4.8	0.016	2.6
PBMA	0.13	0.59	0	100	20	1/1/0.1	4.8	0.0006	a
PBMA	0.13	0.13	0	100	15	1/1/1	10.0	0.0094	1.1
PBMA	0.13	0.30	0	100	15	1/1/1	10.0	0.016	2.6
PBMA	0.13	0.98	0	100	15	1/1/1	10.0	0.048	7
PBMA	0.10	0.64	10	100	15	1/1/1	10.0	0.037	b
PBMA	0.09	0.64	10	80	20	1/1/0.1	4.8	0.0064	b
PBMA	0.04	0.64	10	80	20	1/1/0.1	4.8	0.0023	b
PBMA	0.10	0.64	10	80	20	1/1/0.1	4.8	0.006	b
PBMA	0.10	0.64	10	80	50	1/1/0.1	4.8	0.055	24
PBMA	0.10	0.64	10	90	20	1/1/0.1	4.8	0.014	55
PBMA	0.10	0.64	10	90	50	1/1/0.1	4.8	0.096	16
PBMA	0.10	0.64	10	100	20	1/1/0.1	4.8	0.024	35
PBMA	0.10	0.64	10	100	50	1/1/0.1	4.8	0.14	15
PBMA	0.10	0.64	10	100	100	1/1/0.1	4.8	0.309	11
PBMA	0.10	0.64	10	115	20	1/1/0.1	4.8	0.009	70
PBMA	0.10	0.64	10	120	20	1/1/0.1	4.8	0.005	b
PBMA	0.10	1.64	10	100	22	1/1/0.1	4.8	0.0005	b
PBMA	0.10	0.98	10	100	22	1/1/0.1	4.8	0.012	b
PBMA	0.10	0.64	10	100	22	1/1/0.1	4.8	0.024	b
PBMA	0.10	0.54	10	100	22	1/1/0.1	4.8	0.033	b

Table 3-2. Continued.

Film	[Rh]	delta	P/Rh	Temperature (Celcius)	Pressure (psig)	Gas Mixture (H2/CO/C3H6)	Flow Rate	Activity	n/b Ratio
PBMA	0.10	0.22	10	100	22	1/1/0.1	4.8	0.022	b
PBMA	0.10	0.64	10	100	20	1/1/4	4.8	0.45	b
PBMA	0.10	0.64	10	100	20	1/1/2	4.8	0.057	67
PBMA	0.10	0.64	10	100	20	1/1/1	4.8	0.033	14
PBMA	0.10	0.64	10	100	20	1/1/0.1	4.8	0.018	b
SGR	0.10	0.64	10	80	15	1/1/1	10.0	0.006	b
SGR	0.10	0.64	10	100	15	1/1/1	10.0	0.029	b
SGR	0.10	0.64	10	80	15	1/1/1	10.0	0.006	b
SGR	0.10	0.64	10	80	60	1/1/1	10.0	0.061	44
SGR	0.10	0.64	10	80	80	1/1/1	10.0	0.67	27
PBD	0.10	0.64	10	80	15	1/1/1	10.0	0.085	17
PBD	0.10	0.64	10	100	15	1/1/1	10.0	0.034	b
Aliquat 336	0.10	0.64	10	80	15	1/1/1	10.0	0.01	b
Aliquat 336	0.10	0.64	10	100	15	1/1/1	10.0	0.043	b
TBPCl	0.10	0.64	10	100	15	1/1/1	10.0	0.01	b
PC	0.10	0.64	10	80	15	1/1/1	10.0	0.07	b
PC	0.10	0.64	10	80	15	1/1/0.1	4.8	0.013	b
PC	0.10	0.64	10	100	15	1/1/1	10.0	0.197	41
PC	0.10	0.64	10	100	60	1/1/1	10.0	0.342	11
DEPT	0.10	0.64	10	80	15	1/1/1	10.0	0.29	58
2-Octanol	0.10	0.64	10	80	15	1/1/1	10.0	0.35	4
TNBP	0.10	0.64	10	80	15	1/1/1	10.0	0.14	2.7

Table 3-2. Continued.

Film	[Rh]	delta	P/Rh	Temperature (Celcius)	Pressure (psig)	Gas Mixture (H2/CO/C3H6)	Flow Rate	Activity	n/b Ratio
None	0.10	0.64	10	80	15	1/1/1	10.0	0.019	b
None	0.10	0.64	10	100	15	1/1/1	10.0	0.033	b
None	0.10	0.64	10	100	15	1/1/1	10.0	0.033	b
PEG*		1.40	50	100	20	1/1/0.1	4.8	3.1%	14.3
PEG*		1.40	50	100	40	1/1/0.1	4.8	12.5%	7
PEG*		1.40	50	100	60	1/1/0.1	4.8	14.1%	6
PEG*		1.40	50	120	60	1/1/0.1	4.8	5.3%	9

Rhodium source - HRh(CO)(PPh3)3; Phosphine - Triphenylphosphine.

a - Activity too low to detect additional products.

b - n-Butyraldehyde was the only product detected.

PBMA - Polybutylmethacrylate; SGR - Silicone gum rubber; PBD - Polybutadiene;

TBPCL - Tetrabutylphosphonium chloride; PC - Propylene carbonate; DEPT - diethylenephthalate;

PEG - Polyethylene glycol (MW 600)

None - Film consists of a triphenylphosphine film only.

* - Rhodium source HRh(CO)(TPPTS)3; Phosphine - TPPTS.

Results and Discussion

The system described herein demonstrates the activity of previously reported SLPC but uses a non-volatile "liquid" phase such as a polymer or molten salt. Polymer or molten salt films are non-volatile and should retard the sublimation of the transition metal catalyst or phosphines in the film.

Several polymers and molten salts were chosen as reaction media for the supported catalysts, these include polybutylmethacrylate (PBMA), polybutadiene (PBD), silicone gum rubber (SGR), aliquat 366 and tetrabutylphosphonium bromide. The transition metal complex, hydridocarbonyltristriphenylphosphine rhodium(I), was chosen as the catalyst, for its high activity, selectivity, and stability in homogenous catalytic systems. Silica gel was chosen as the support for its porosity, and high surface area.

Calculations

The activities (α) were calculated in units of TON/min, where TON is the turnover number defined as the number of moles of products formed (n_p) per mole of catalyst (n_c), eq. 3-1. The value of n_p can be calculated by multiplying the

$$\alpha(TON/\text{min}) = \frac{n_p}{n_c} \qquad \text{(eq. 3-1)}$$

conversion to products, σ_p, by the moles of substrate, n_s, (n_p and n_s are in units of

moles/min). The moles of substrate, n_s, can be calculauted via the ideal gas law

$$n_p - \sigma_p n_s \qquad \text{(eq. 3-2)}$$

(equation 3-3.). The pressure of the substrate, P_s, is measured at the gas outlet. The value V_{fr} is the flow rate, R is the gas law constant and T is the temperature at the sample loop. It should be noted that the flow rate is incorporated into the activity.

$$n_s = \frac{P_s V_{fr}}{RT} \qquad \text{(eq. 3-2)}$$

In hydroformylation the selectivity is the percentage of the products which are aldehydes. Included in this term is the ratio of normal to branched aldehydes (n/b ratio). Occasionally the equivalent term linear to branched or l/b is used. This value is calculated from the calibration corrected area for the two aldehyde products. In this work many of the catalysts gave only one isomer product, the linear aldehyde.

Hydroformylation in Thin Films

The question of activity in thin polymeric films was addressed in our labs by utilization of hydroformylation catalysts immobilized in polymer films.[58] In previous work, the rhodium complexes $HRh(CO)(PPh_3)_3$ and $(tfa)Rh(PPh_3)_4$ (tfa=trifluroacetylacetonate) were placed in a polymer membrane and tested for the hydroformylation of propylene at 85°C and 15 psig. These systems were moderately active and the activities and selectivities could be influenced by altering the polymer media. A polystyrene membrane catalyst yielded a system which produced 1×10^{-9} mol

of butyraldehyde in 3 days with a n/b of 0.71. Changing the polymer matrix to the rubbery polymer polybutylmethacrylate produced a system that increased in activity to 2.2×10^{-7} mol in one day and the selectivity was an amazing 500:1. Figure 3.9 is a schematic of the reactor used in these experiments.

It was suspected that diffusion of the reactant gases (syn gas and propylene, 1:1:1 gas mixture) through the polymer matrix was the limiting effect in the membrane reactor. In order to increase the surface area of the catalytic film we supported these films on inorganic oxides. This forms a thin catalytic film over the support which should decrease the diffusion time of the reactants through the polymer. In addition, the resultant catalyst is a dry powder that can be easily handled in the air for a short period of time.

Polymers and Triphenylphosphine/Polymer Films

Polybutylmethacrylate films

A catalyst containing $HRh(CO)[P(C_6H_5)_3]_3$, and polybutylmethacrylate (PBMA) was dispersed on silica gel. The catalysis was carried out in a gas flow reactor, using premixed gases of hydrogen, carbon monoxide and propylene. This catalyst was considerably more active than the unsupported membrane reactor systems. The supported polymer film catalyst had an activity of 0.016 TON/min (conditions 100°C, 20 psig, flow rate 10mL/min, δ = 0.25) and a n/b of 2.6:1, while the membrane reactor showed an activity of 4.17×10^{-5} TON/min under similar conditions.
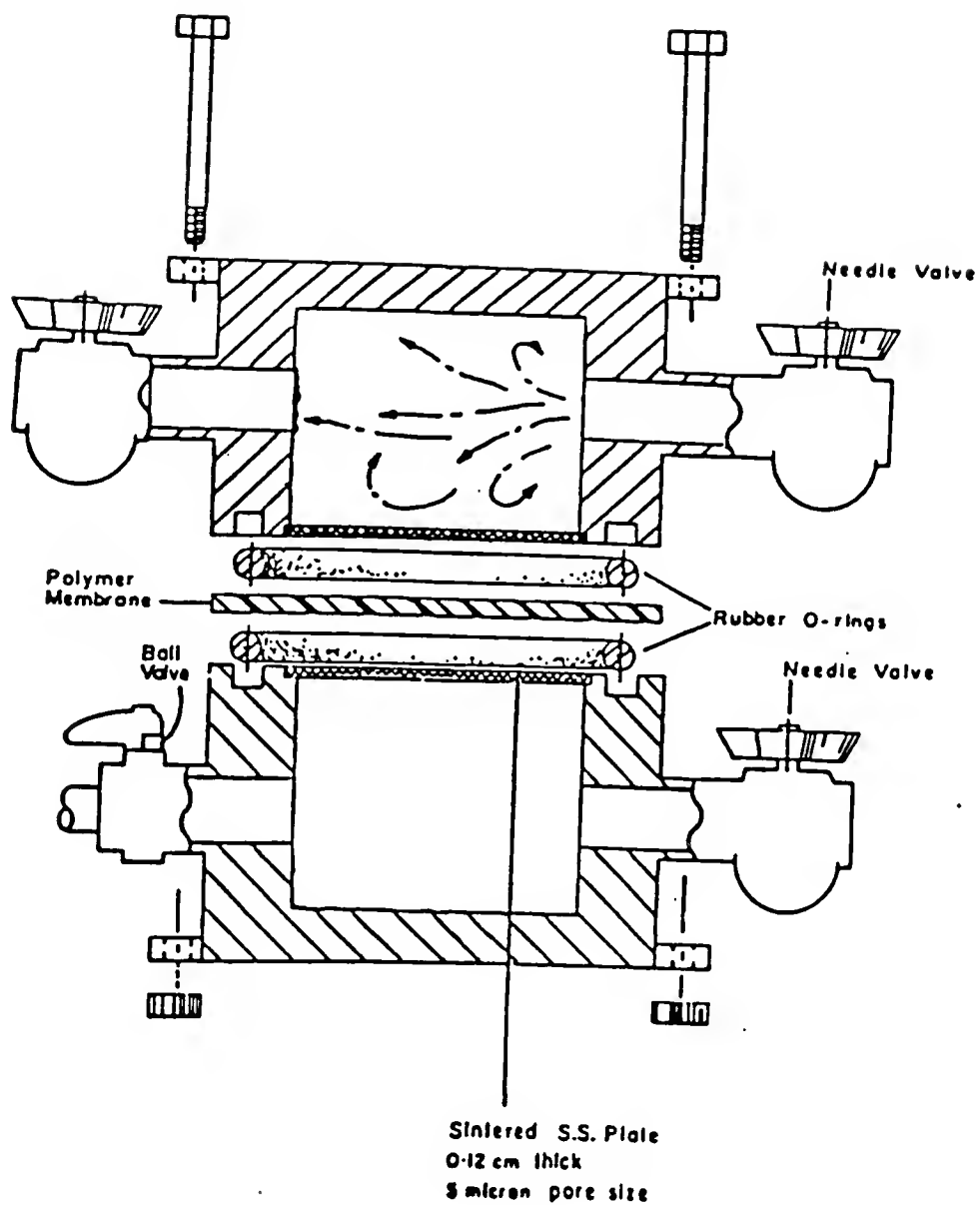
Needle Valve

Polymer
Membrane

Rubber O-rings

Ball
Valve

Needle Valve

Sintered S.S. Plate
0·12 cm thick
5 micron pore size

Figure 3-9.   Thin film membrane reactor.

A PBMA catalyst, with a degree of pore filling, δ, of 0.59 showed an activity of 6×10^{-4} TON/min. The selectivity could not be determined due to the low activity. This film represents a relatively thick coating on the support surface. The activity is considerably lower than the other catalyst. Figure 3-10 depicts the activity curves for these experiments. This effect can be attributed to the rigid nature of PBMA films. Although the polymer is above its glass transition temperature ($T_g = 80°C$) at a reaction temperature of 100°C, the polymer is not liquid, but solid. This restricts free movement of the catalyst and makes diffusion of the reactant gases rate limiting.

Concentration effects. The effects of rhodium concentration within the supported film was tested. It was found that increasing the concentration of rhodium in the film increased the activity and the selectivity of the catalysts despite the increased degree of pore filling (the effects of pore filling on this system will be discussed in greater detail vida infra) (see Table 3-3 and Figures 3-11 and 3-12). The activity increased with increasing rhodium concentration.

Polybutylmethacrylate/triphenylphosphine films

It has been long realized that the addition of excess phosphine ligands to the rhodium catalyst increases the lifetimes and stability of the catalysts. We decided to add triphenylphosphine to the PBMA film to stabilize the rhodium complex. With this addition we observed an unexpected increase in activity to 0.0373 TON/min, this is approximately twice that of the previous catalyst. In addition, the system produced only n-butyraldehyde, the desired linear product. This increase in activity was
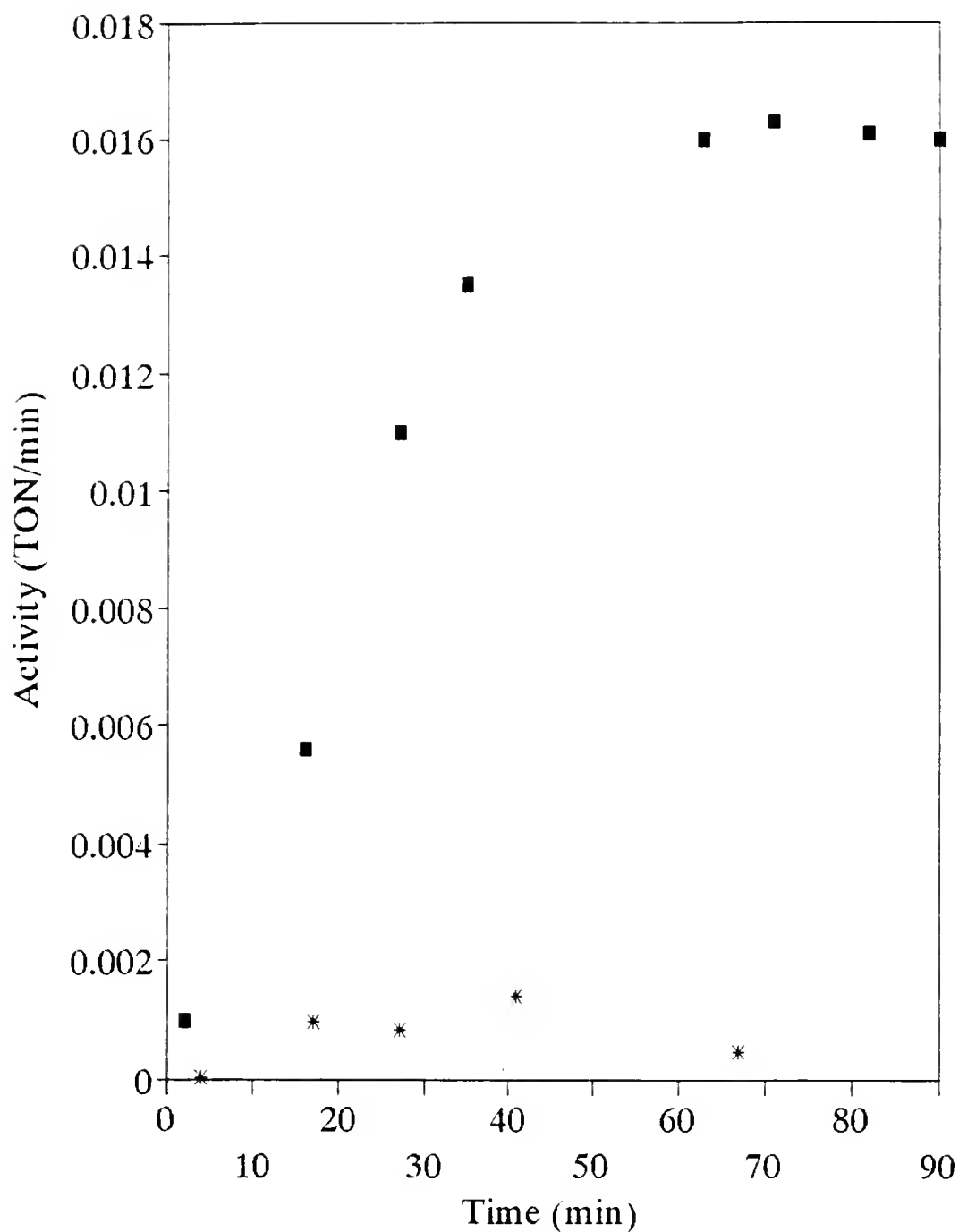
.

Figure 3-10. Activity of the PBMA film catalyst for the hydroformylation of propylene. ■-δ = 0.25. + - δ + 0.59.
Catalyst: Rhodium source-HRh(CO)(PPh$_3$)$_3$; P/Rh - 10:1; Polymer-PBMA.Conditions: 80°C, 15 psig (1:1:1 H$_2$/CO/propylene).

Table 3-3.   Effects of Change in Concetration of the Rhodium Source.

[Rh]x10^4 (mmol Rh/ml film)	Activity (TON/min)	n/b
0.25	.0090	1
1.00	0.023	2.5
2.60	0.058	7.0

Catalyst: HRh(CO)(TPP)$_3$; Polymer: PBMA; Additive: None. Conditions: 100°C, 15 psig (1:1:1 H$_2$/CO/propylene); Flow rate: 10mL/min.
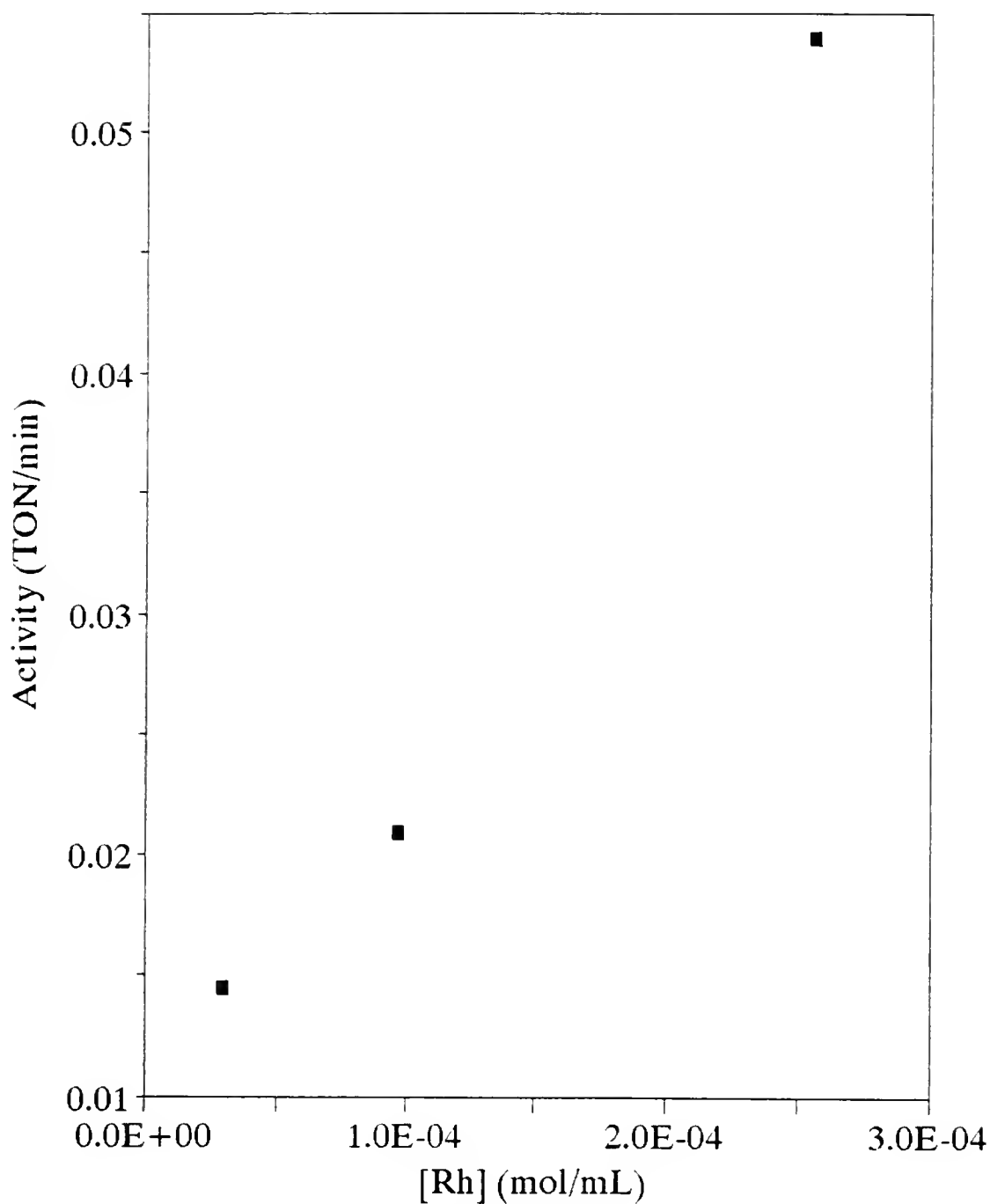
Figure 3-11. Effects of changing rhodium concentration on the activity for the hydroformyaltion of propylene.
Catalyst: Rhodium source-HRh(CO)(PPh$_3$)$_3$; Polymer-PBMA.
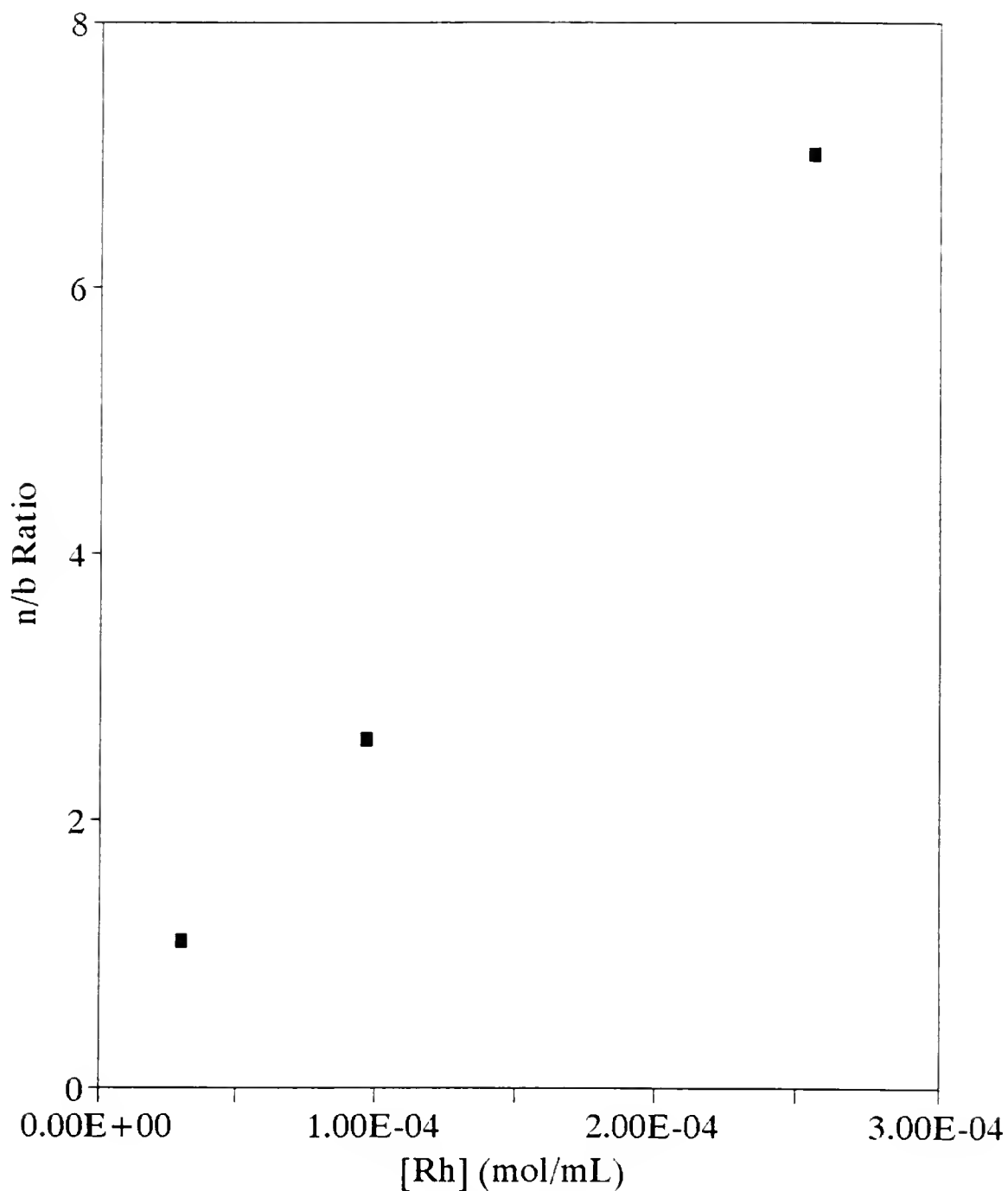Conditions: 80°C, 15 psig (1:1:1 H$_2$/CO/propylene).

Figure 3-12. Effects of changing rhodium concentration on n/b ratio for the hydroformylation of propylene.
Catalyst: Rhodium source-HRh(CO)(PPh$_3$)$_3$; Polymer-PBMA.
Conditions: 80°C, 15 psig (1:1:1 H$_2$/CO/propylene).

attributed to the loosening of the film by molten triphenylphosphine (melting point 81°C). This the film should be more mobile than one consisting of PBMA alone. Table 3-4 shows the activity and selectivity of several catalysts involving PBMA.

The concentration of rhodium within the film was varied while holding both δ and the percentage of PBMA relative to triphenylphosphine constant. Increasing the rhodium concentration from 0.040 gRh/g of film to 0.090 gRh/g of film considerably increased the activity, while not significantly influencing the selectivity (see Table 3-5).

Effects of temperature and pressure. As expected, the activity of PBMA/PPh₃ systems increase with increasing temperature (see Table 3-6). For systems at 50 psig of reactant gas (1:1:1 H_2/CO/propylene) an increase of activity was observed from 0.060 TON/min at 80°C to 0.14 TON/min at 100°C. At 20 psig similar effects were observed (0.0064 TON/min, 80°C; 0.024 TON/min, 100°C). The energy of activation for this system was calculated to be 52.1 $\pm$ 11 kJ/mol at 50 psig and 68.15 $\pm$ 11 KJ/mol at 20 psig (see Figures 3-13 and 3-14). These values are the same with in the error limits.

Similar increases in activity are seen with pressure. At 80°C and 20 psig the activity is 0.0064 TON/min and is totally selective to n-butyraldehyde. Increasing the pressure to 50 psig increases the activity to 0.055 TON/min, while the selectivity drops to 24. A further increase to 100°C and 100 psig brings the activity to 0.309 TON/min and a n/b of 11.

Table 3-4.   Selected Catalysts for the Hydroformylation of Propylene.

Support	Film	Activity (TON/min)	Selectivity
silica	PBMA	1.60×10^{-2}	2.62
none	PBMA	1.1×10^{-10}	a
silica	PBMA/TPP	3.73×10^{-2}	b
silica	TPP	3.29×10^{-2}	b

a- Trace amounts of isobutyradehyde were formed.
b- n-Butyradehyde was the only product detected.
Rhodium   source: $HRh(CO)(TPP)_3$.   Conditions: 100°C,   15   psig   (1:1:1
H_2/CO/propylene), Flow rate 10 mL/min.

Table 3-5.   Effect of Concentration of the Rhodium Source in the PBMA/Triphenylphosphine Film.

[Rh] (g Rh/g film)	δ	Activity[a] (TON/min)
0.090	0.64	0.0064
0.040	0.64	0.0023

[a] Both catalyst produced n-butyradehyde exclusively.
Catalyst: $HRh(CO)(PPh_3)_3$; Polymer: PBMA; P/Rh = 10:1. Conditions: 80°C, 20 psig (1:1:0.1 H_2/CO/propylene), flow rate of 4.8 mL/min.

Table 3-6.   Effects of Temperature and Pressure on the Hydroformylation of Propylene using the PBMA/Triphenylphosphine Film Catalyst.

Temperature (°C)	Pressure (psig)	Activity (TON/min)	n/b Ratio
80	20	0.006	[a]
80	50	0.055	24
90	20	0.014	55
90	50	0.096	16
100	20	0.024	35
100	50	0.140	15
100	100	0.309	11
115	20	0.009	70
120	20	0.005	[a]

[a] n-Butyraldehyde was the only product detected.

Gas mixture 1/1/0.1 H_2/CO/propylene; Flow rate 4.8 mL/min.

Catalyst: Rhodium source - $HRh(CO)(P\phi_3)_3$; P/Rh = 10:1; [Rh] = 0.10 g Rh/g catalyst; δ = 0.64.
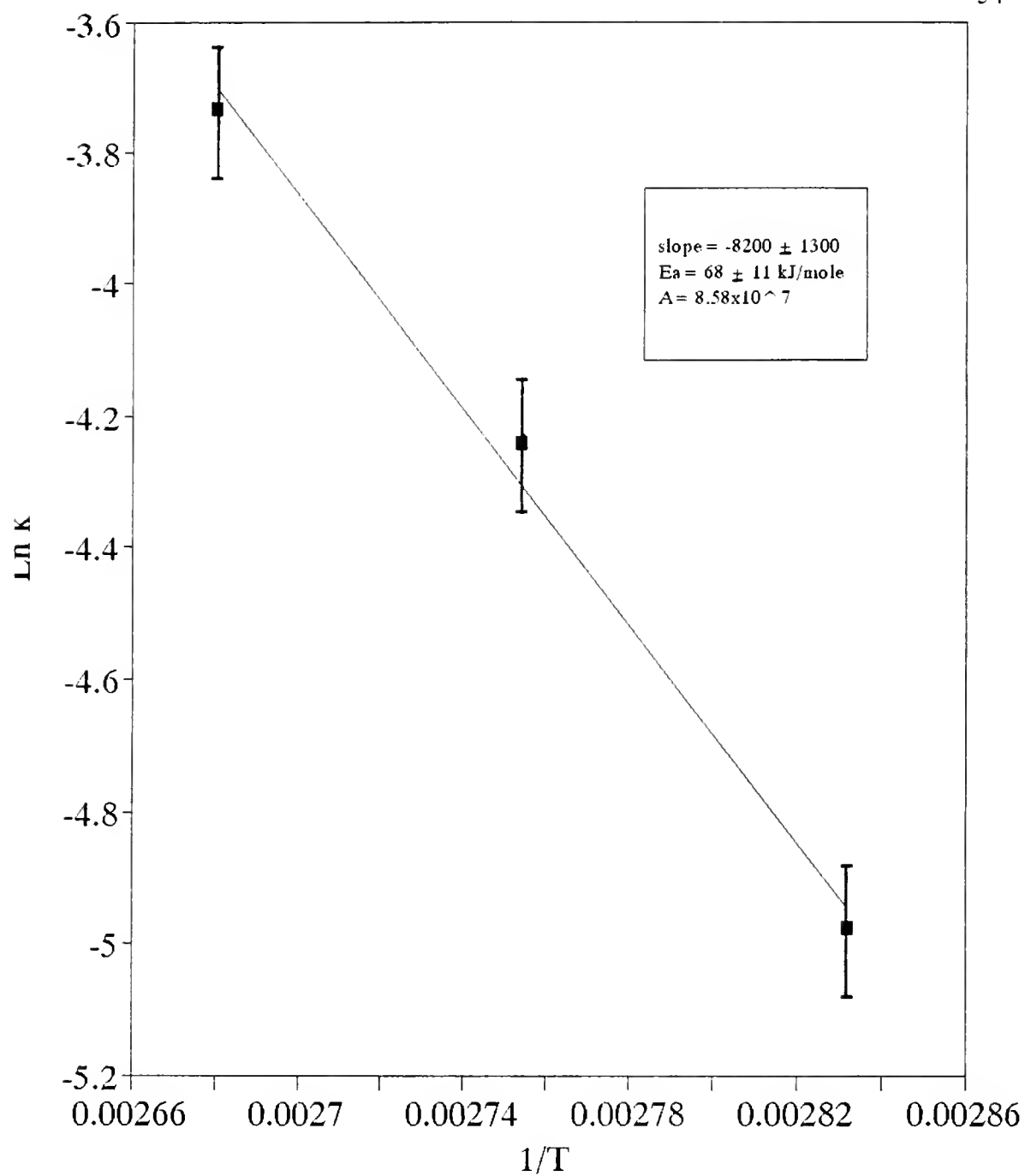
Figure 3-13.   Arrhenius plots for the PBMA catalyst at 20 psig. Temperature range
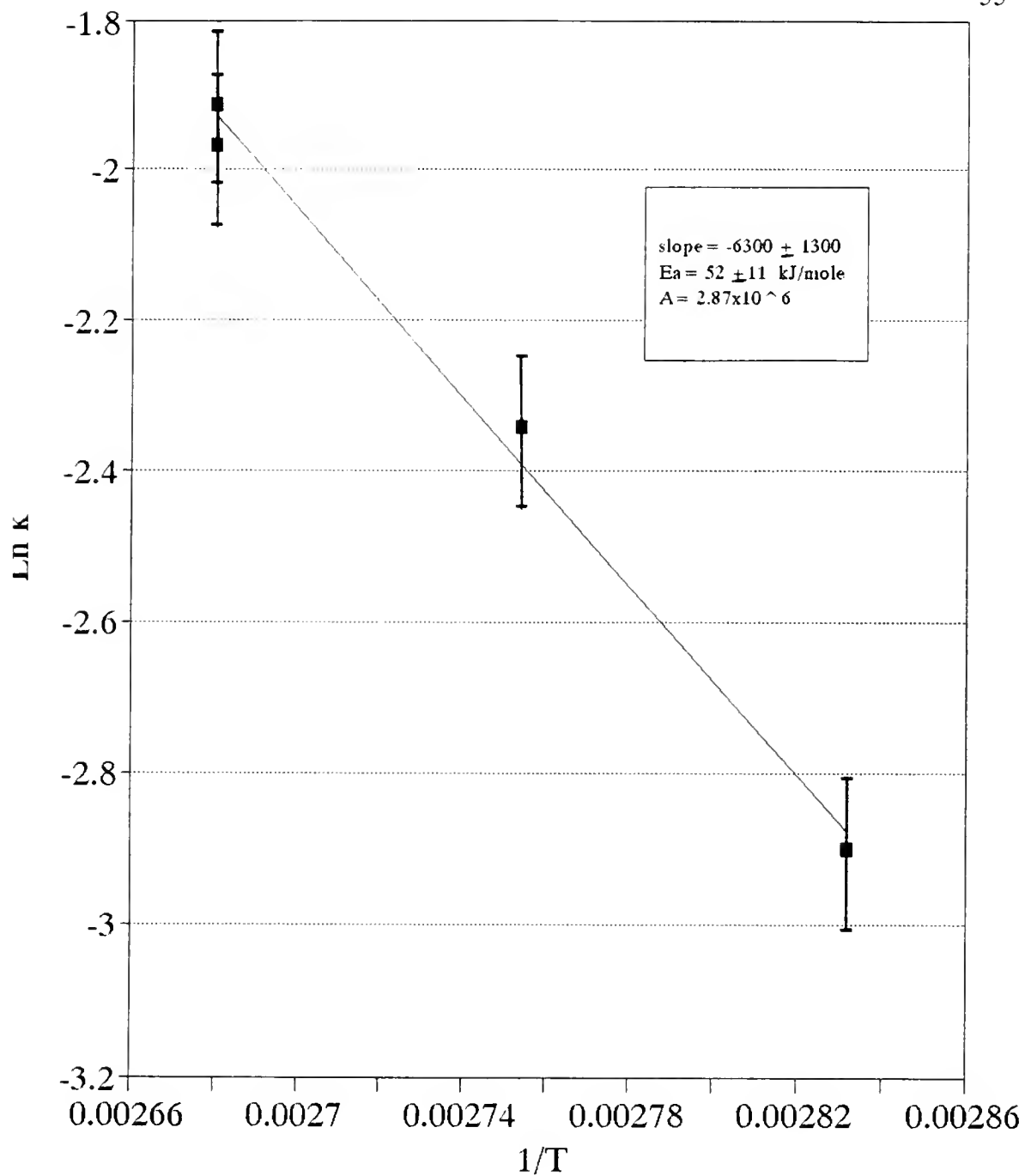80°C to 100°C.

Figure 3-14. Arrhenius plots for the PBMA catalyst at 50 psig. Temperature range 80°C to 100°C.

Influence of phosphine to rhodium ratio

Dependence of activity and selectivity on the ratio of free phosphine to rhodium complex was studied. A trend developed that showed selectivity increasing with increasing P/Rh ratio. This is expected from similar results in homogeneous systems with these catalysts. The role of excess triphenylphosphine in homogeneous systems is to enhance the stability and lifetime of the catalyst. With only triphenylphosphine as the film, the selectivity increases with increasing P/Rh ratio (Figure 3-15). The addition of PBMA to the film increases the n/b ratio dramatically at lower P/Rh ratios.

Effects of pore filling

The effect of the degree of pore filling of film was studied. Table 3-7 and Figure 3-16 shows a drop in catalyst activity with increasing δ, while the n/b ratio increased. The loss in activity can be easily explained by the decrease in surface area. Since the film is a solid most of the active species are at the gas/film interface, and any rhodium complex in the interior of the film would be inactive. Hence a reduction in surface area equates to fewer active species and a decrease in the overall activity.

Effects of propylene feed

It was noticed that varying the composition of the gas feed greatly effects the activity of the catalyst (see Table 3-8). In several cases, an increase in propylene feed increased the overall activity. At a gas mixture of 1/1/4 (H_2/CO/propylene) the
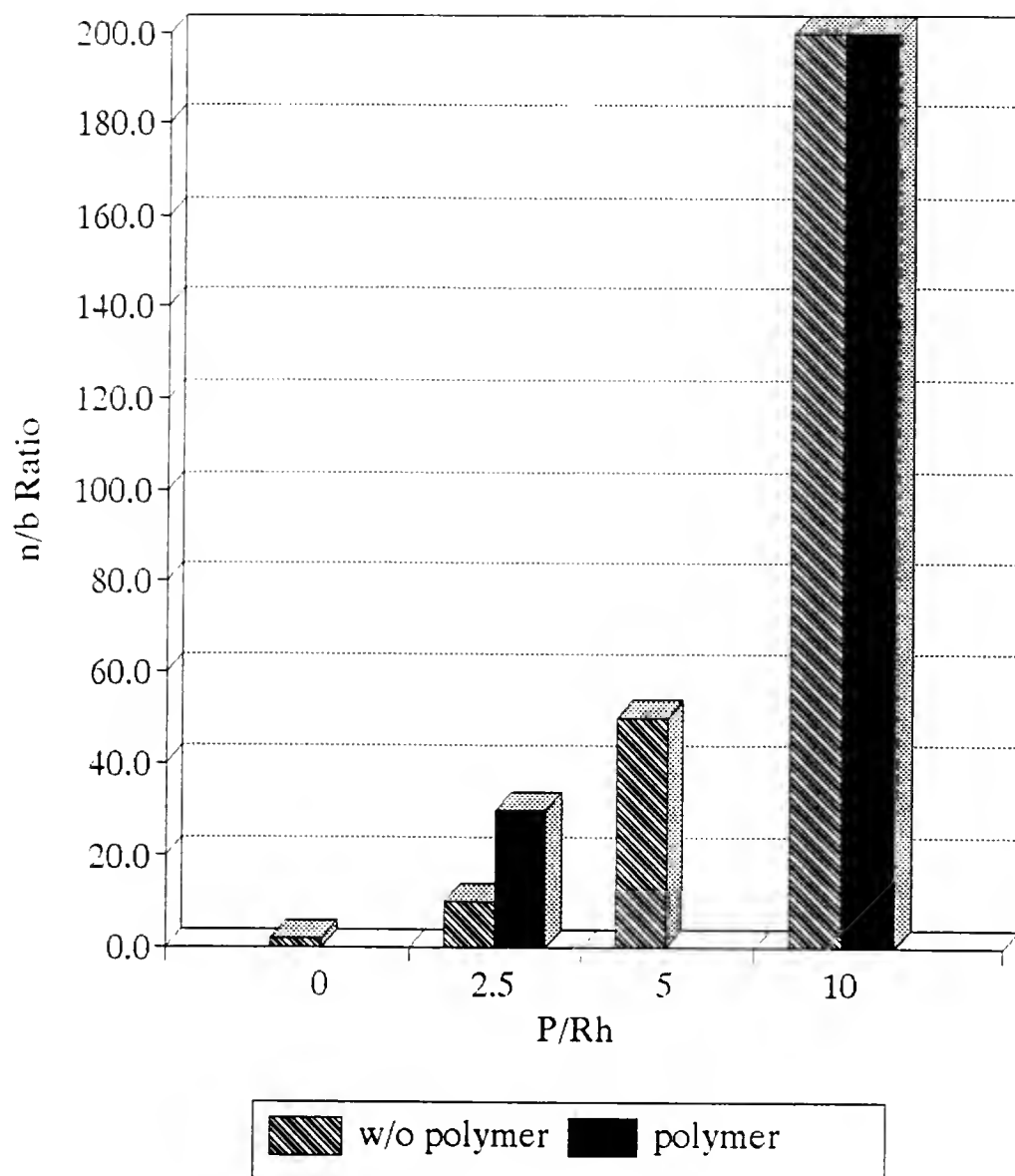
Figure 3-15. Change in selectivity with variing P\Rh ratio.
Catalyst: Rhodium source-HRh(CO)(PPh$_3$)$_3$; δ = 0.64.
Conditions: 80°C, 15 psig (1:1:1 H$_2$/CO/propylene).

Table 3-7.   Effects of Pore Filling (δ) on the Activity of the PBMA Film
Catalytic System.

δ	Activity (TON/min)	n/b Ratio
1.64	5.0×10^{-4}	[b]
0.98	0.012	[a]
0.64	0.024	35
0.54	0.033	[a]
0.22	0.022	21

[a] -n-Butyraldehyde was the only product detected.
[b] -Activity was below the detection limit for isobutyraldehyde.
Catalyst: HRh(CO)(TPP)$_3$; Polymer: PBMA;
               P/Rh = 10; [Rh] = 0.1 g of Rh per g of catalyst.
Conditions: 100°C, 22 psig (1:1:0.1 H$_2$/CO/propylene),
               flow rate of 10mL/min.
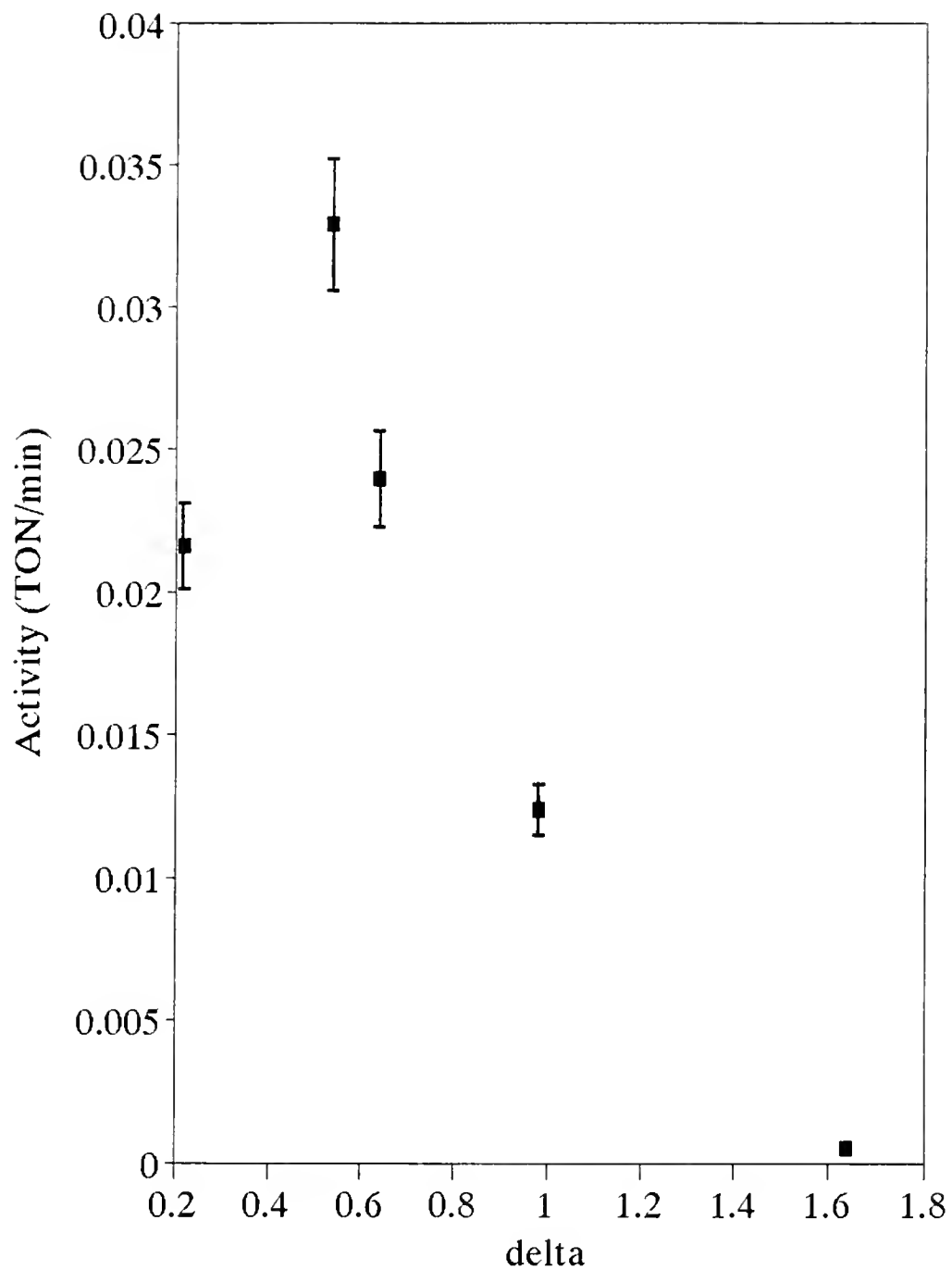
Figure 3-16. Effects of filling the pores with catalytic film on the activity of propylene hydroformylation. Catalyst: Rhodium source - HRh(CO)(PPh$_3$)$_3$; P/Rh=10:1; [Rh] = 0.11; Polymer-PBMA. Conditions: 80°C, 15 psig (1:1:1 H$_2$/CO/propylene).

Table 3-8.   Effect of Pregas Mix/Propylene Concentration on the Activity and Selectivity of the Hydroformylation of Propylene.

Gas mixture	Activity (TON/min)	Selectivity
1/1/4	0.450	a
1/1/2	0.057	67
1/1/1	0.033	14
1/1/0.1	0.018	a

a. n-Butyradehyde was the only product detected.

Catalyst: Rhodium source - $HRh(CO)(PPh_3)_3$; Polymer - PBMA; P/Rh = 10:1; δ = 0.64: [Rh] = 0.11.

Conditions: 100°C, 20 psig (1:1:x H_2/CO/propylene), flow rate = 4.8 mL.min.

activity was 0.45 TON/min. Mixtures of 1/1/1 gave 0.0325 TON/min. At low propylene concentration (1/1/0.1) the activity was 0.0175 TON/min. This would indicate that at low propylene feeds the polymer phosphine films are not being saturated with enough propylene to get optimal conversion.

Selectivity is also affected by the amount of propylene in the gas mixture. It was evident that the higher the concentration of propylene in the feed the higher the selectivity.

Effects of flow rates

Since the concentration of propylene plays an important role in the activity of a catalyst, the flow rate of the reactant gases should also effect the rates. At a flow rate of 10 mL/min (80°C, 50psig) the activity was 0.257 TON/min, while the selectivity was 2.2. Upon reduction of the flow rate to 4.8 mL/min the activity drops to 0.055 TON/min and the selectivity increases to 24:1. It should be noted that calculation of the activity includes flow rate as one of the terms. Table 3-9 and Figure 3-17 shows the steady increase of activity with flow rate at 100°C and 20 psig.

Other polymer films

Silicone gum rubber (SGR) and polybutadiene (PBD) were tested as films for STFC. These rubbery polymers will produce a more mobile film than PBMA. Under similar conditions, the SGR catalyst was less active than its PBMA counterpart [at 20 psig and 80°C (0.006 TON/min and 0.015 TON/min respectively)] (see

.

Table 3-9.   Activities of PBMA Film Catalyst for the Hydroformylation of Propylene at Various Flow Rates.

Flow Rate (mL/min)	Activity (TON/min)
0.96	0.007
4.80	0.018
7.20	0.032
9.60	0.031
17.76	0.071
19.20	0.062

Conditions: 100°C, 20 psig.
Pregas: 1/1/0.1 H_2/CO/propylene
Catalyst: Rhodium source - HRh(CO)(Pϕ_3)$_3$; P/Rh - 10:1;
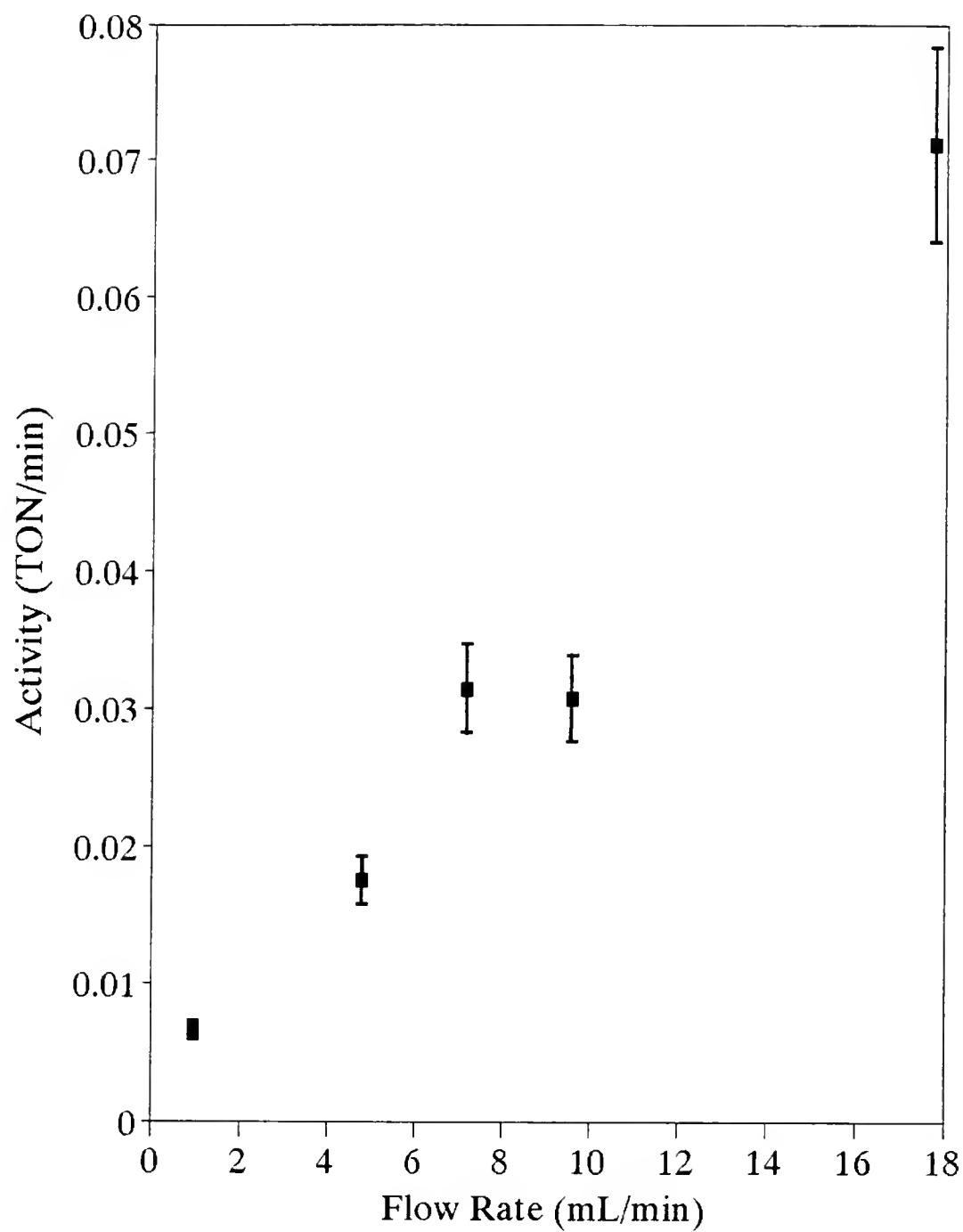   [Rh] = 0.10 g Rh per g catalyst.

Figure 3-17. Effects of flow rates on the activity of the PBMA film catalyst on the hydroformylation of propylene.

Table 3-10 and Figure 3-18), and was very selective producing only n-butyraldehyde. Two possibilities exist for the decrease in activity: 1) The non-polar nature of the SGR may decrease the solubility of hydrogen, carbon monoxide and propylene; 2) The silicon polymer may simply poison the catalyst.

The PBD system was considerably more active (0.81 TON/min) than either SGR or PBMA, with no apparent loss in activity over a two hour period. The catalyst produced predominately n-butyraldehyde in a 17:1 n/b ratio. Polybutadiene is very rubbery under reaction conditions and possesses no functionalities which would poison the catalyst. Polybutadiene does, however, posses olefinic functionalities which may be hydroformylated. Analysis of the film was not done but if this reaction is occurring the film does not deactivate the catalyst. Reactions at these internal olefinic sites on the polymer is expected to be much slower than the rate of reaction for the hydroformylation of propylene. This lower activity coupled with the large excess of propylene used in the reaction should minimize the possibility of hydroformylation of the polymer alkene units.

Comparisons of activity with temperature and pressure. Figure 3-18 demonstrates the differences in activity of the three polymer systems at 80°C. The polybutadiene film catalyst was the most active followed by PBMA and SGR. Table 3-11 and Figure 3-19 shows that at 100°C all the polymers are equivalent in activity. This could be due to loosening of the films by molten triphenylphosphine. Triphenylphosphine has a melting point of 80°C. At 100°C triphenylphosphine will be molten and contribute significantly to the film. Table 3-12 shows the expected

Table 3-10. Comparison of Polymers as   Films for the Hydroformylation of Propylene with SLPC's at 80°C.

Film	Activity (TON/min)	n/b Ratio
PBMA	0.015	[a]
SGR	0.006	[a]
PBD	0.085	17
None	0.019	[a]

[a] The only product detected was n-butyraldehyde.
Conditions: 80°C, 15 psig (1:1:1 H_2/CO/propylene).
Catatalyst: Rhodium source - $HRh(CO)(P\phi_3)_3$; P/Rh ratio - 10:1; [Rh] = 1.0 x 10^{-4} mol Rh per gram catalyst; δ = 0.64; mass of catalyst = 0.50 g.
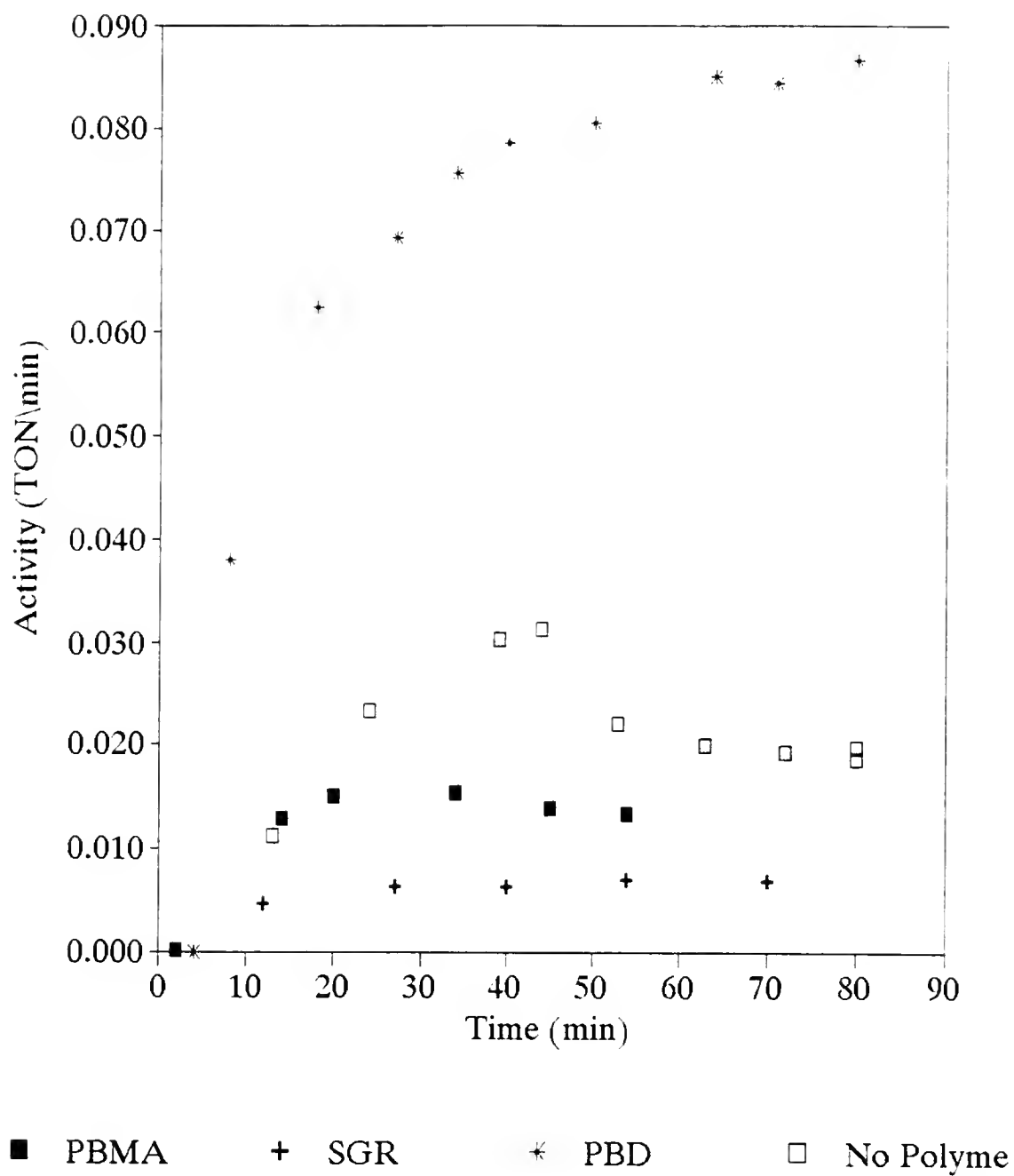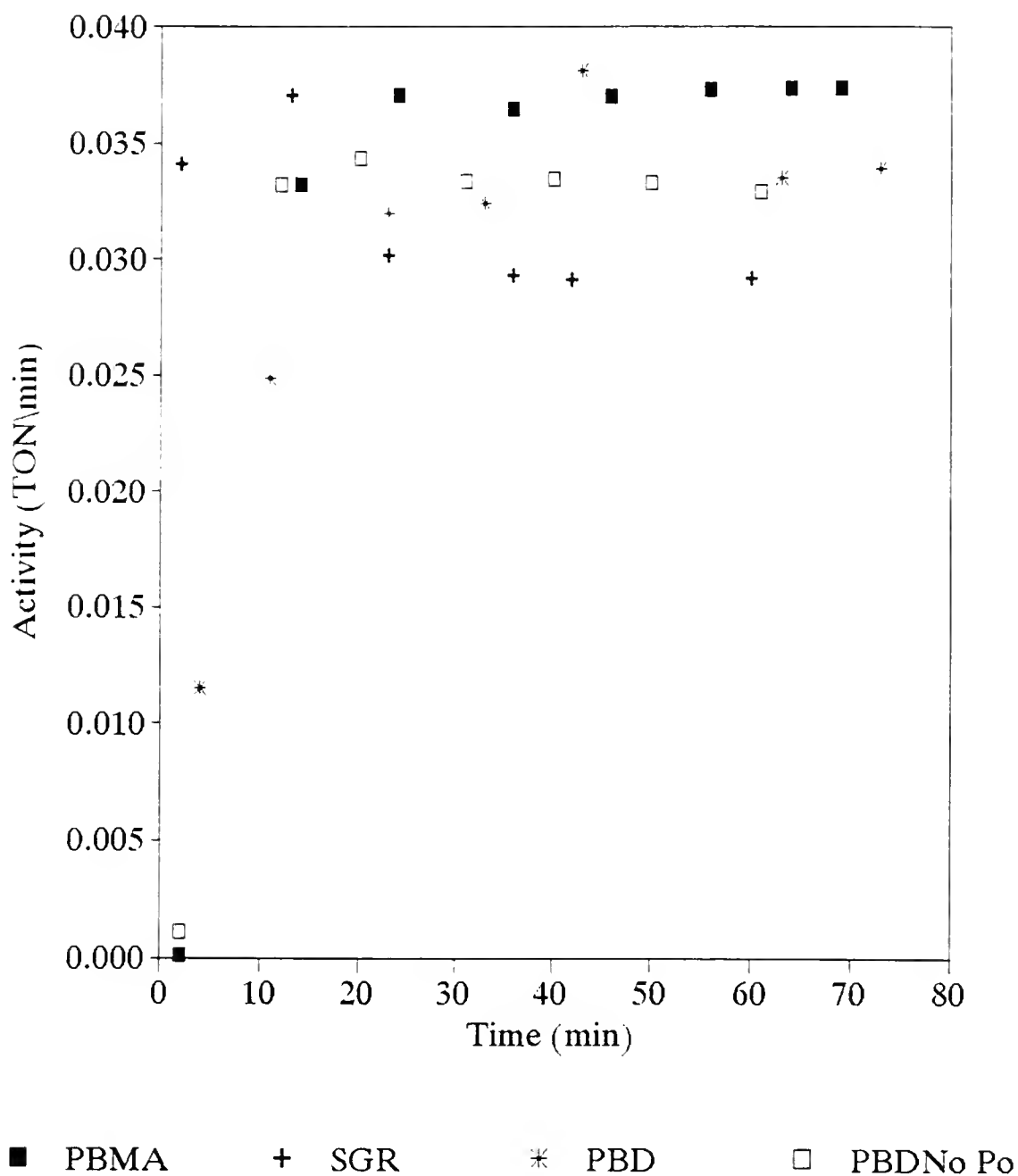
Figure 3-18. Activity curves of several supported polymer film catalysts for he hydroformylation of propylene at 80°C. Catalyst: Rhodium source-HRh(CO)(PPh₃)₃;P/Rh = 10:1; δ = 0.64.
Conditions: 80°C, 15 psig (1:1:1 H₂/CO/propylene).

Table 3-11. Comparison of Polymers as Films for the Hydroformylation of Propylene with SLPC's at 100°C.

Film	Activity (TON/min)	n/b Ratio
PBMA	0.037	[a]
SGR	0.029	[a]
PBD	0.034	[a]
None	0.033	[a]

[a] The only product detected was n-butyraldehyde.

Conditions: 100°C, 15 psig (1:1:1 H_2/CO/propylene).

Catatalyst: Rhodium source - $HRh(CO)(P\phi_3)_3$; P/Rh ratio - 10:1; [Rh] = 1.0 x 10^{-4} mol Rh per gram catalyst; δ = 0.70; mass of catalyst = 0.50 g.

Figure 3-19. Activity curves of several supported polymer film catalysts for he hydroformylation of propylene at 100°C. Catalyst: Rhodium source-HRh(CO)(PPh₃)₃;P/Rh = 10:1; δ = 0.64.
Conditions: 100°C, 15 psig (1:1:1 H₂/CO/propylene).

Table 3-12.   Effects of Varired Pressure with a SGR Film Catalyst.

Temperature (°C)	Pressure (psig)	Activity (TON/min)	n/b Ratio
80	15	0.006	[a]
80	60	0.061	44
80	80	0.670	27

[a] n-Butyraldehyde was the only product.

Gas mixture: 1/1/1 H_2/CO/propylene; Flow rate = 10 mL/min.

Catalyst: Rhodium Source - HRh(CO)(PPh$_3$)$_3$; P/Rh = 10:1;
                    [Rh] = 0.10 g Rh per g CAtalyst; δ = 0.64.

increase in activity and decrease in n/b ratio for the SGR film catalyst with the increase in pressure.

Alternative Films

Molten salts

Molten salts are candidates as liquid phase media[59], both aliquat 336 (tri-n-octyl methyl ammonium chloride) and tetrabutylphosphonium bromide demonstrate similar activity to their polymer counter parts at loadings and conditions comparable to the polymer systems (see Table 3-13). These systems produced only n-butyraldehyde and showed no loss in activity over a three hour period. Both Aliquat 336 and tetrabutylphosphonium chloride are molten at room temperature.

As in the case of polymer films, an increase in reaction temperature does increase the overall activity of the system. At 80°C the activity of the aliquat 366 catalyst is 0.010 TON/min and increases at 100°C to 0.044 TON/min. Both catalysts only produce n-butyraldehyde.

Liquid films

Supported liquid phase catalysts were tested as control catalysts for hydroformylation of propylene. The liquids examined were 2-octanol, diethylene phthalate, and propylene carbonate. These catalysts were run as simulants to Rony's SLPC and to test if the totally selective systems found with rubbery polymers and molten salts were real phenomena or a product of the flow rates and pressures of the

Table 3-13.   Hydroformylation of Propylene with Molten Salt Film Catalysts.

Film	Conditions (°C/psig)	Activity (TON/min)	n/b Ratio
Aliquat 336	80/15	0.010	[a]
Aliquat 336[b]	80/15	0.046	[a]
Aliquat 336	100/15	0.044	[a]
TBPCl	100/15	0.010	[a]
PBMA	100/15	0.038	[a]

[a] n-Butyraldehyde was the only product detected.
[b] δ = 1.31, [Rh] = 0.06 g Rh per g catalyst.
Reactant gas 1:1:1 H_2/CO/propylene, flow rate = 10 mL/min.
Catalyst: Rhodium source - $HRh(CO)(PPH_3)_3$; P/Rh 10:1; [Rh] = 0.1 g Rh per g catalyst.

gas flow reactor used in the experiment. As expected, all the high boiling liquid catalysts showed slightly higher catalytic activity toward aldehydes than their polymeric counterparts. In addition to higher activity, the production of iso-butyraldehyde was appreciable (see Table 3-14).

Several experiments were carried out with propylene carbonate under our relatively mild conditions for the purpose of comparison with the polymer systems. It was determined that increasing temperature and pressure generally increase the activity while lowering the selectivity (see Table 3-15).

Other Vapor Phase Substrates

In addition to propylene, 1-butene and 1,3 butadiene are of interest as substrates. We have tested these substrates with the $HRh(CO)(PPh_3)_3$/PPh$_3$/PBMA/SG catalyst at 100°C and 20 psig. But-1-ene shows both the linear and branched products in a 15.7:1 ratio, and a activity of 0.084 TON/min. Buta-1,3-diene produced four products with conversions approaching 0.173 TON/min.

Hydroformylation of Propylene with Supported Hydrophilic Catalysts

The hydroformylation of liquid alkenes such as 1-hexene will be described in the following chapter. In this section we will describe the hydroformylation of propylene with the catalyst used for liquid alkenes. The catalyst consists of a water soluble rhodium catalyst $(HRh(CO)(TPPTS)_3)$ (TPPTS = $P(C_6H_4SO_3Na)_3$) and excess

Table 3-14. Hydroformylation of Propylene with Various SLPC's.

Film	Activity (TON/min)	n/b Ratio
Diethylenephthalate	0.29	58.0
2-Octanol	0.35	4.0
Tri-n-butylphosphate	0.14	2.7
Propylene carbonate	0.07	a
PBMA	0.037	a

a The only product was n-butyraldehyde.

Conditions: 80°C, 15 psig 1:1:1 H_2/CO/propylene. Flow rate = 10 mL/min.

Catalyst: Rhodium source - $HRh(CO)(PPh_3)_3$; P/Rh = 10:1;
[Rh] = 0.10 g Rh per g catalyst.

Table 3-15.   Hydroformylation of Propylene with Various Propylene Carbonate Film Catalysts.

Temperature (°C)	Pressure (psig)	Gas Mixture ($H_2/CO/C_3H_6$)	Activity (TON/min)	n/b Ratio
80	15	1/1/1	0.007	[a]
80	15	1/1/0.1	0.013	[a]
100	15	1/1/1	0.197	41
100	60	1/1/1	0.342	11

[a] The only product detected was n-butyraldehyde.

Conditions: Flow rate = 10mL/min.

Catalyst: Rhodiun source - $HRh(CO)(PPh_3)_3$; P/Rh = 10:1;
                    [Rh] = 0.10 gRh per g catalyst; δ = 0.64.

ligand (TPPTS) in a water soluble polymer (PEG 600) coating silica gel (see Table 3.16). The degree of pore filling for this catalyst was 1.40. At 100°C and 20 psig of 1:1:0.1 H_2/CO/propylene this catalyst showed a conversion of 0.114 TON/min and a selectivity of 14.3. An increase in pressure to 40 psig increased the activity to 0.461 TON/min but lowered the n/b ratio to 6.69. A further increase in pressure raised the activity to 0.519 and a n/b of 5.83. Increasing the temperature to 120°C decrease the activity to 0.196 and increased the selectivity to 8.74.

This demonstrate the feasibility of the water soluble rhodium catalyst in a hydrophilic film coating silica for the hydroformylation of vapor phase substrates such as propylene. The activity of this system is high for the degree pore filling ($\delta = 1.4$). Further experiments with lower δ's should be done.

Conclusions

We developed a novel approach to supported liquid phase catalyst which uses a polymer or molten salt as the film phase. These catalysts consist of a rhodium source ($HRh(CO)(PPh_3)_3$ in a polymer or molten salt film supported on silica gel. Previously reported SLPC used high boiling liquids as the liquid phase, leading to films that evaporate with time, leaving a surface supported rhodium catalyst. We have seen that the addition of excess phosphine ligand (triphenylphosphine) to the catalytic film enhances the activity and the selectivity of the overall catalyst. This enhancement can be attributed to the loosening of the film by molten triphenylphosphine in the film, at temperatures above 80°C.

Table 3-16.   Hydroformylation of Propylene with a Supported Hydrophilic
               Catalyst.

Temperature (°C)	Pressure (psig)	Conversion (%)	Activity (TON/min)	n/b Ratio
100	20	3.1	0.114	14.3
100	40	12.5	0.461	6.69
100	60	14.1	0.519	5.83
120	60	5.3	0.196	8.74

Catalyst: Rhodium source - $HRh(CO)(TPPTS)_3$; Additive: TPPTS;
               Polymer: PEG 600; Support: Silica gel; $\delta = 1.4$.
Pregas mixture: 1/1/0.1 H_2/CO/propylene, flow rate 4.8 mL/min.

We have varied a number of the conditions and film properties of the catalytic system and found that even a slight modification of any of the variables affects the activity of the system dramatically. They include temperature, pressure, degree of pore filling and concentration of rhodium in the film. It was shown that increased temperature and pressure increased activity but decreased selectivity of the catalyst, while the activity decreased significantly with the increase in pore filling. The concentration of rhodium in the film also had an effect on the activity; as the concentration increased so did the activity and the selectivity.

We also varied the film material by using different polymers and molten salts. All of the films tested were active for the hydroformylation of propylene. The molten salts tested showed extraordinary selectivity by producing only the linear aldehyde. Liquid films such as propylene carbonate, 1-octanol and diethylene phthalate demonstrated higher activities than their polymer counterparts but much lower selectivities.

The catalyst system described herein has shown to be an effective system for the hydroformylation of vapor phase substrates under mild conditions. The following chapter will describe a system for the hydroformylation of liquid substrates in a batch reactor.

CHAPTER 4
HYDROFORMYLATION OF HIGHER OLEFINS WITH SUPPORTED HYDROPHILIC FILM CATALYSTS

Introduction

The goal of heterogenizing homogenous catalysts is to design a catalyst that would have many of the advantages inherent in both heterogeneous and homogenous catalytic systems. Homogeneous catalysts offer high activity and selectivity along with the ease of modification of the system. Heterogeneous catalysts offer the ease of separation of the catalyst from the reactants and products along with the easy recovery of expensive transition metals.

Many heterogeneous catalysts have been developed for hydroformylation. Most include the coordination of rhodium or cobalt to functionalized organic polymers or inorganic oxides. The functionalized groups are usually phosphines. In addition, catalysts have been trapped in zeolites and several biphasic systems have been developed.

Supported Transition Metal Catalysts

Organic polymers. Numerous polymer-supported transition metal systems have been developed and studied for catalysis.[60,61,62] Organic polymers which contain pendant phosphines have been prepared. The major drawback to these

catalysts is the elution of rhodium from the polymer surface.[63,64] Pittman et al. have chemically linked rhodium, cobalt, ruthenium and nickel complexes to polymers via phosphine coordination. The polymer-bound transition metal catalysts were efficient catalysts for cyclooligomerization, hydrogenation, and hydroformylation.[52,65,66] The catalysts are depicted in Figure 4-1.

The rhodium phosphine polymer hydroformylated 1-pentene at 250-1000 psi and 40-60°C yielding a n/i ratio of 2.5:1.[67,68] Comparison of the rhodium catalyst to the homogeneous catalyst, $HRh(CO)[P(C_6H_5)_3]_3$, under similar conditions gave interesting results. At low temperatures, 40°C, the activity of the polymer catalyst was significantly lower than the homogeneous catalyst. However, when the temperature was increased to 60°C, the activity of the two catalysts were nearly identical. This phenomena was explained by diffusion of the reactants through the polymer matrix. At lower temperatures the chains are restricted and immobile. The increase in temperature decreased the viscosity of the resin which in turn greatly reduced the diffusion time of the reactants to the rhodium centers.

After extended reaction time the activity of the catalyst decreased but time while the n/b ratio increased. As the reaction is allowed to proceed the rhodium center becomes more highly coordinated by anchored phosphines leading to low activities and high n/b ratios. A later study showed that in catalysts with high loadings of anchored phosphines a high degree of substitution results and n/b ratios of 12:1 are observed. Low loadings of anchored phosphines gave n/b ratios similar to those of homogeneous catalysts.
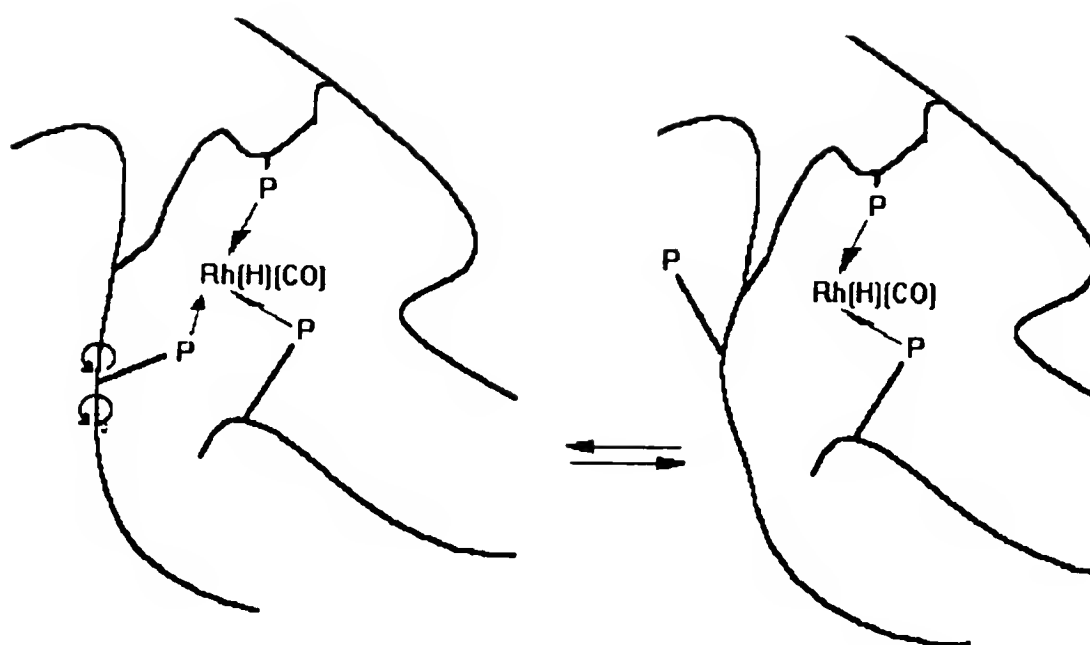
Figure 4-1. Coordination of rhodium to a polymer support via pendant phosphine ligands.

Allum et al. developed similar polymer supports shown in Figure 4-2.[69] Rhodium catalysts can be made by the addition of Rh(acac)(CO)$_2$ to the polymer. These copolymers are efficient hydroformylation catalysts for 1-hexene at 90°C and 42 atm (1:1 H$_2$/CO) but n/b ratios are low (0.81). Treatment of these polymers with tri-n-butylphosphine increases the ratio to 2.3:1. In a continuous flow reactor (pilot plant conditions) the activity of this catalyst drops dramatically from 86% to 36% within 10 hours, but selectivity remains unchanged at 2.5:1. Leaching of the catalyst into the reaction feed occurs. Trace amounts of oxygen facilitates metal leaching from the support.

Non-phosphine containing polymer supports coordinate rhodium to produce active hydroformylation catalysts. The polymer contains a organic sulfide group for the linkage to the transition metal.[70] This catalyst converts 100% of the 1-hexene over an 8 hour period and has a n:i ratio of 1.

Inorganic oxides. Numerous inorganic oxides can be used as supports for hydroformylation catalysts (e.g. silica gel, alumina, and porous glass).[71] Direct deposition of RhCl$_3$ or (PPh$_3$)$_2$Rh(CO)Cl lead to catalysts which show negligible activity for the hydroformylation of 1-hexene at 100°C and 300 psig.[76] At low pressures these catalysts are efficient isomerization catalysts for the formation of 2-hexene. Increasing pressure and temperature gives an active catalyst for the hydroformylation of propylene.

Allum et al supported metal complexes on silica by reacting HRh(CO)[(EtO)$_3$SiCH$_2$SiCH$_2$CH$_2$PPh$_2$]$_3$ with functionalized silica.[47] Under pilot plant

Preparation via susbstituted polystyrenes
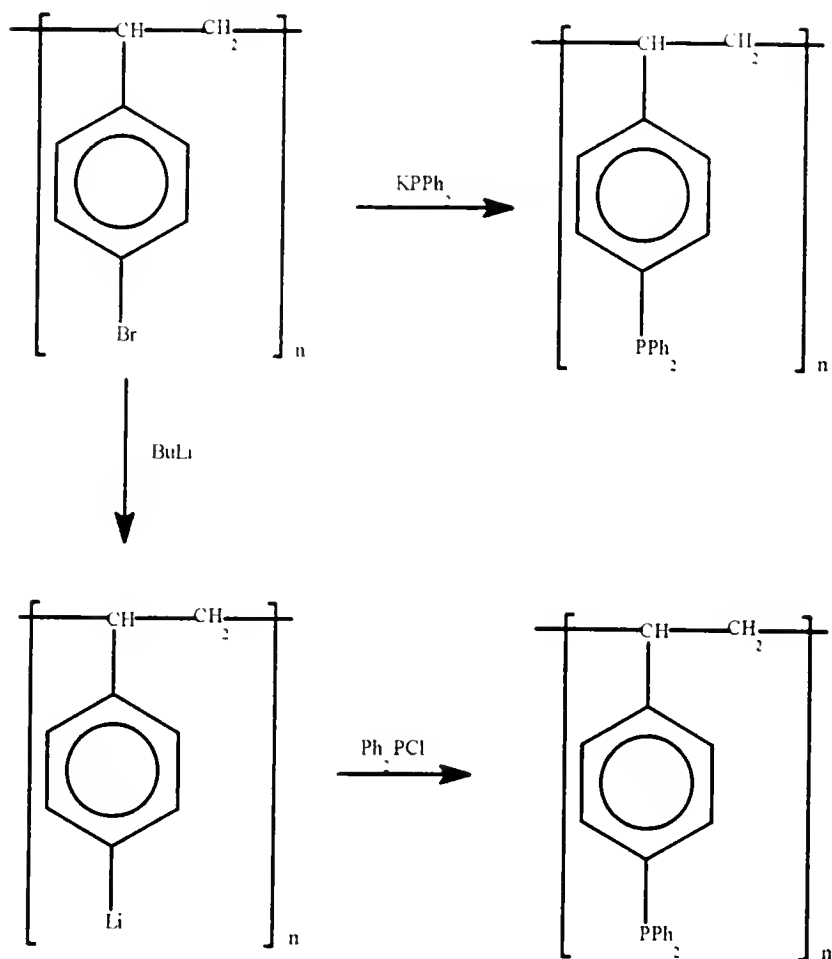
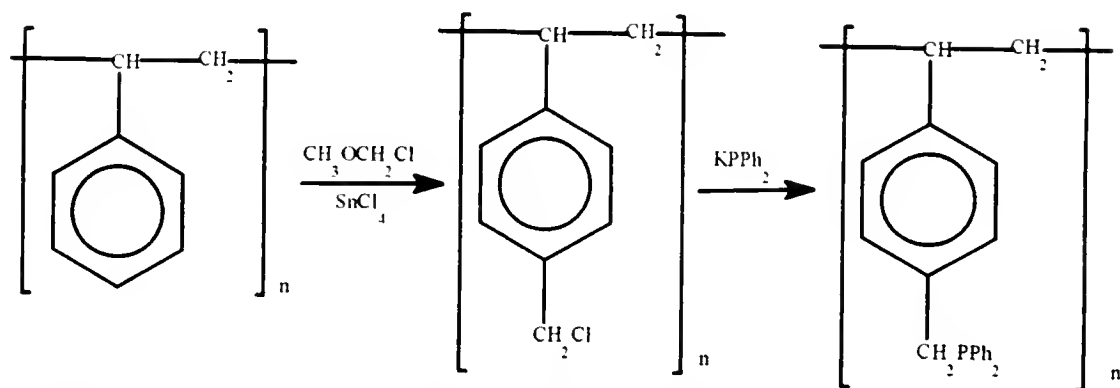# Prepation via unsubstituted polystyrenes

Figure 4-2. Preparation of functionalized polymers.

conditions the catalyst leaches into the feed initially but after the first few hours no further leaching occurs. The leaching can be attributed to the presence of trace amounts of oxygen in the reaction solution.

Zeolites. Various rhodium complexes can be incorporated into zeolites.[72,73,74] Only a few are useful as heterogeneous catalysts for liquid substrates.[75] The main drawback to zeolite supported catalysts is the leaching of the rhodium complex into the reaction solution. Never the less, there have been a few catalyst which are active for the hydroformylation of 1-hexene and do not elute rhodium into the solution.[76]

Davis and coworkers have described the various types of zeolite catalysts for hydroformylation in which the rhodium source is cation exchanged into the zeolite.[77] There are three fashions in which the rhodium can be bound to the support. For type I the rhodium species is weakly bound to the surface of the support and easily elutes into solution. For type II the active species is tightly bound to the zeolite support. The activities of these sites are low, because the rate is diffusion limited. Type III has the rhodium complex entrapped within the zeolite cage. The n/b ratio for type III sites are reported to be 2.6:1.

Biphasic catalysts

A variety of water soluble ligands and complexes are used for biphasic catalysis.[78,79,80] These systems employ the use of immiscible solvents to achieve the desired separation characteristics of heterogeneous catalysts[81,82] and rely heavily on the solubility of the substrates in the phase in which the catalyst resides. Sulphonate

phosphines are commonly used as ligands for rhodium complexes in biphasic catalytic systems.[83] Rhone-Poulenc utilizes the water soluble catalyst, $HRh(CO)(TPPTS)_3$ (TPPTS=trisodium tris(m-sufonatophenyl)phosphine), and the water soluble ligand, TPPTS, for the hydroformylation of propylene.[84,85,86] The metal complex and excess ligand resides in the aqueous phase while the majority of the substrates (propylene) and products (n-butyraldehyde and isobutyraldehyde) are in the organic phase. Efficient conversions of the olefin are made with a n:i ratio of 3:1. A similar system uses a chelating sulfonated phosphine as a ligand for rhodium catalysts. These systems yield high activities at low P/Rh ratios.[87]

Other biphasic hydroformylation systems have appeared. Taqui Khan et al. report a system which exclusively produces n-heptaldehyde from 1-hexene using Ru-EDTA in a 80/20 ethanol-water mixture at 130°C and 50 atm.[88] A rate of 11.8 TON/hr is achieved and the catalyst can be recycled with out loss of activity.

Baird et al have developed a rhodium water soluble catalyst with using the ammonium phosphine ligand $Ph_2PCH_2CH_2NMe^+NO_3^-$.[89] An active catalyst for hydroformylation can be made with [(norbornadiene)RhCl]$_2$ in the presence of the phosphine, (at least a 3:1 P/Rh ratio). The active catalyst is [(norbornadiene)Rh(Ph$_2$PCH$_2$CH$_2$NMe)$_2$]$^{3+}$ and hydroformylates 1-hexene which is dissolved in hydrophobic organic solvents. An n:i ration as high as 4:1 is observed, the selectivity is dependant upon the choice of solvent. Small amounts of hydrogenation and isomerization products were observed, and leaching of a small amount of rhodium into the organic media occurred.

The addition of surfactants such as CTAB or quantinary ammonium salts increases the efficiency of the biphasic rhodium catalyst (see Table 4-1).[90] A biphasic system that consists of $PPh_2C_6H_4CO_2H$, and a rhodium source in water converts 2% of the 1-hexene substrate in three hours. With the addition of a surfactant, the conversion increases to 44% in one hour. It was also noticed that high selectivity occurs with poor mixing.

Supported Aqueous Phase Catalysts

Recently, supported aqueous phase catalysts (SAPC) have been developed by Davis et al.[91,92,93] This system covers an inert porous support, such as porous glass, with a thin aqueous film containing a water soluble catalyst, $HRh(CO)(TPPTS)_3$, and a water soluble phosphine, TPPTS. Hydroformylation of higher olefins such as 1-octene and oleyl alcohol can be done at moderate rates and a selectivity of 2.3:1 (conditions:75°C, 700 psig). It is claimed that the rhodium complex is mobile within the aqueous film and the catalysis occurs at the water/organic interface where the organic phase contains the reactants and products.

The rate of hydroformylation is unaffected by the size of the olefin in the SAPC catalyst, whereas in biphasic systems the rate is highly dependent on this variable.[94] This indicates that water evaporates from the surface and leaves a phosphine-rhodium complex bound to the support via hydrogen bonding of the hydrated sodium-sulphonate groups to the surface (see Figure 4-3).

Table 4-1.   Effects of Surfactants on the Biphasic Hydroformylation of Olefins.

Surfactant	Substrate	Time (hours)	% Conversion	n/i
None	1-Hexene	3	2	7
$C_{12}H_{25}N^+Me_3Br^-$	1-Hexene	1	44	73
None	1-Dodecene	3	2	6
$C_{12}H_{25}N^+Me_3Br^-$	1-Dodecene	1	78	20
none	1-hexadecene	3	0.5	-
$C_{12}H_{25}N^+Me_3Br^-$	1-hexadecene	1	73	22

Conditions: $[Rh]_{aq}=300$ ppm, $4\text{-}Ph_2PC_6H_4COOH$, P:Rh=10:1,
$C_{12}H_{25}NMe_3Br$:Rh=20:1 in pH 10 buffer at 80°C, 5.5 atms 1:1 H_2:CO
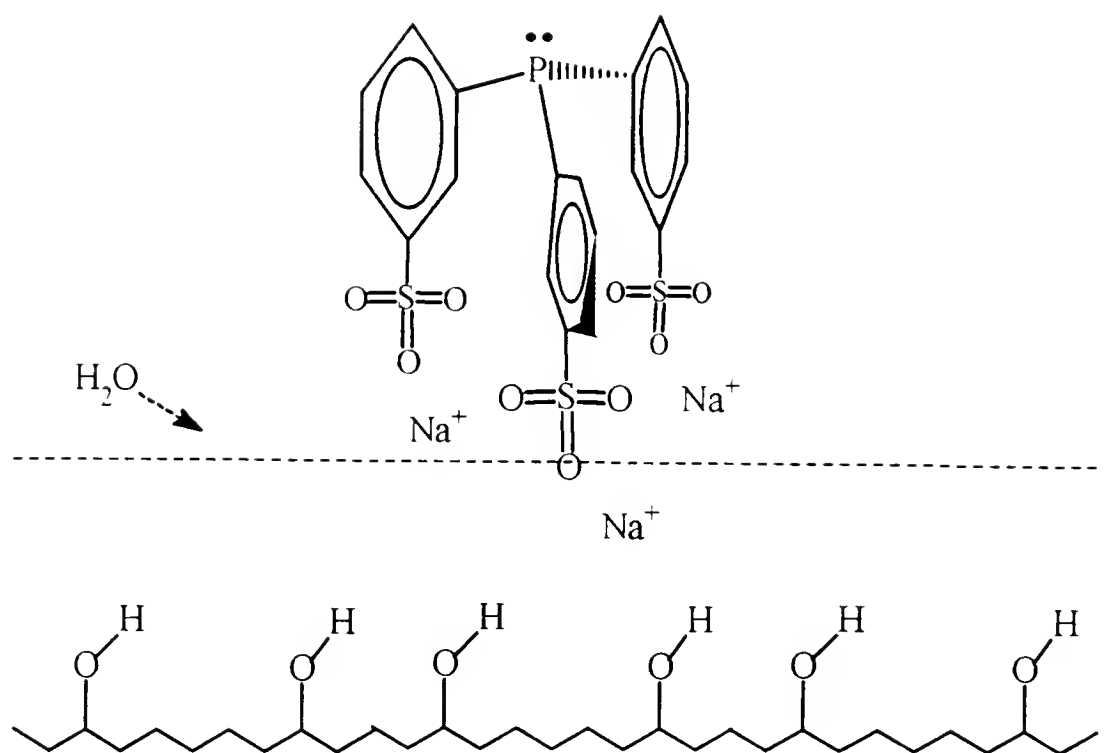
Figure 4-3. Immobilized TPPTS on a hydrophilic support by hydrogen bonding of the hydrated sodium-sulphonate groups to the surface.

Experimental

Chemicals

Water was purified by nanopore filtration and stored under nitrogen. The premixed syn gas were prepared using a manifold system. A lecture bottle was pressurized to 500 psig with carbon monoxide and then pressurized to 1000 psig with hydrogen. The substrates 1-hexene, 1-octadecene, and 1-octene were purchased from Aldrich Chemical and filtered through acidic alumina before use. Valeraldehyde was filtered through acidic alumina and freshly distilled before use. Silica gel (grade 62, mesh 60-200, surface area 700 m^2g^{-1}, pore volume 1.1 mL/g) was purchased from Davison and was dried at 100°C overnight, and sealed under nitrogen. The following were used without any further purification: $Rh(acac)(CO)_2$ (Strem Chemical); $RhCL_3\delta3H_2O$ (Strem Chemical); 2-octanone (Fluka); polyvinyl alcohol (Fluka); absolute ethanol (Florida Distillery Co.); formamide (Aldrich Chemical); polyethylene glycol (Aldrich Chemical) polyvinyl pyrrolidinone (Polysciences Inc.).

Apparatus and Instrumentation

Catalysis was run in either a 300 mL Parr mini reactor or in glass pressure bottles equipped with a pressure head (see Figures 4-4 and 4-5). Nuclear magnetic resonance spectra were obtained by using a Varian VXR 300MHz or a General Electric QE300 nuclear magnetic resonance (nmr) spectrometer. Infrared spectra were obtained from a Nicolet 5PC FTIR spectrometer. Gas chromatographs were obtained by using a Varian 3300, a Perkin-Elmer 900 and a Hewlett Packard 5890 using a DEGS packed column. GC-MS were obtained by using a Varian 3400 equipped with a Finnagan MAT ion trap detector.
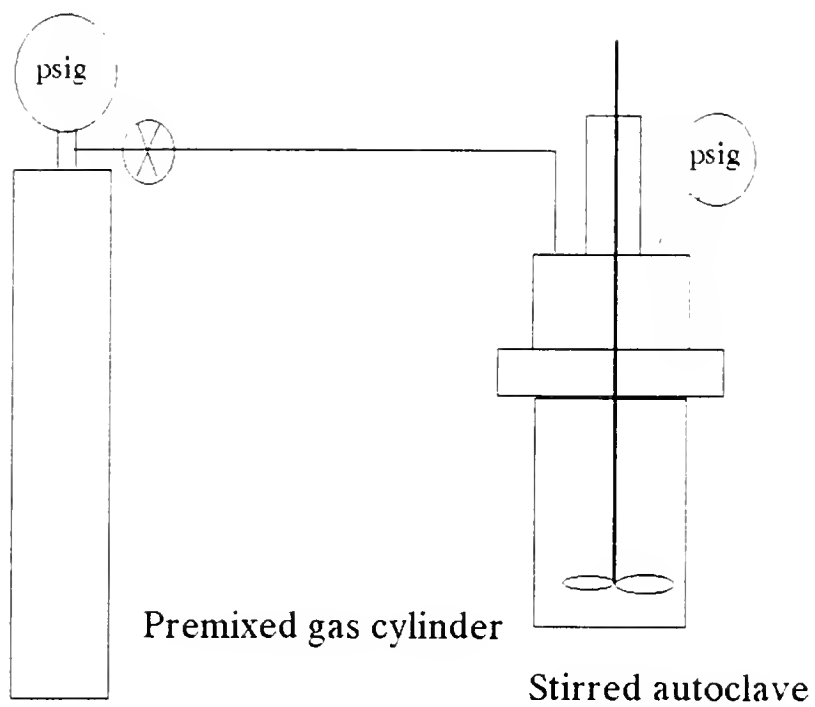
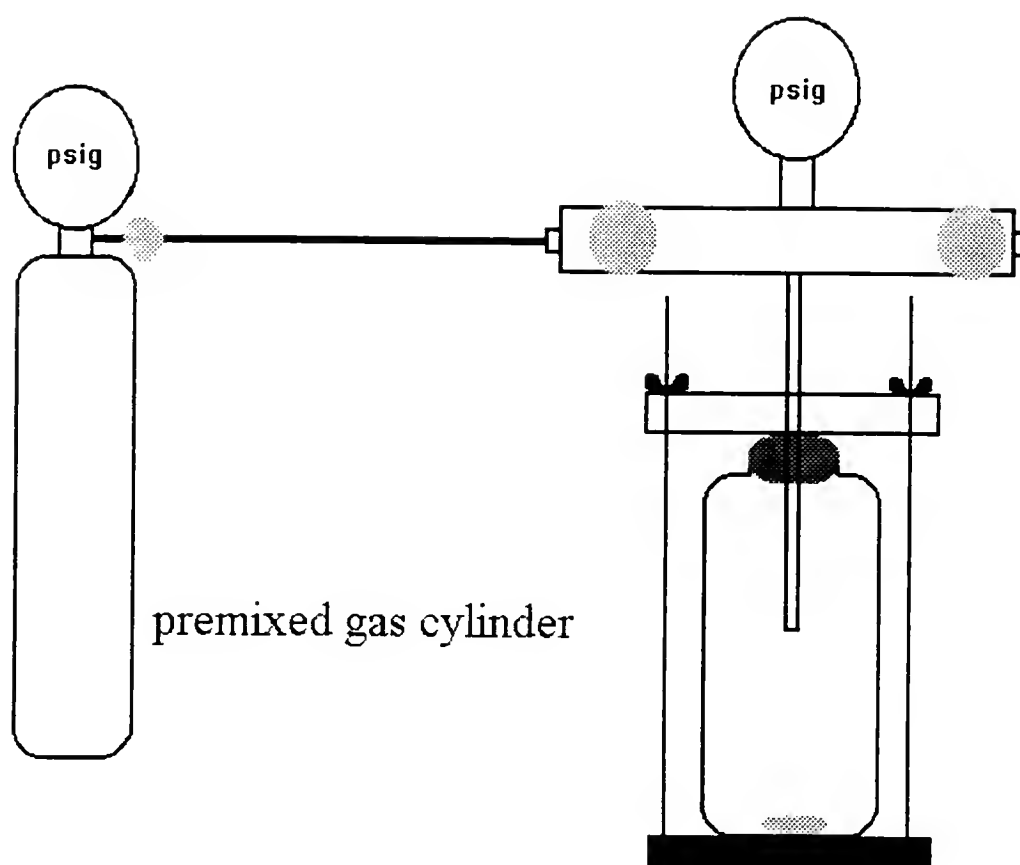Figure 4-4. Parr High Pressure Reactor.

Figure 4-5.   Parr pressure bottle batch reactor.

Synthesis

All manipulations were carried out under an atmosphere of nitrogen.

Preparation of TPPTS

The preparation of TPPTS was carried out similarly to the preparation reported by Arhancet.[92] Oleum (50 mL, 20%) was added dropwise to triphenylphosphine (8.0g) in a three neck round bottom flask cooled by an ice bath. After the addition and complete dissolution of the phosphine, the ice bath was allowed to warm to room temperature and stirring was continued for at least 18 hours (the longer the phosphine solution is allowed to stir the higher the degree of sulfonation). The solution was then cooled to 0-10°C. Cooled deaerated water (200 mL) was added dropwise to the solution to quench the reaction. The acidic phosphine was extracted from the aqueous solution by the addition of tri-n-butylphosphate (50 mL, two times). The organic layers (top) were combined and placed in an ice bath. Concentrated sodium hydroxide (50g, 100 mL) was added dropwise to the acidic phosphine solution until neutral. This resulted in the formation of a white precipitate, from this a white solid forms. The solid was filtered, washed with diethylether (50 mL, 5 times) and air dried. The solid was then taken up in water (75 mL) and methanol was added to precipitate a white solid (mostly Na_2SO_4). The solid was removed by filtration and the filtrate was evaporated under reduced pressure. Phosphorous (^{31}P) nmr of the solid indicated the presence of TPPTS (-5.50 ppm, 82%), HTPPTS (1.69 ppm, 16%) and OTPPTS (36.11 ppm, 3%).

Barium nitrate test of the solid was positive for the presence of Na_2SO_4. The solid was taken up in water (50 mL) and the Na_2SO_4 was precipitated by the addition of absolute ethanol (80 mL). Recrystalization from methanol with ethanol removed all of the phosphine impurities. If any HTPPTS remains it can be removed by washing the solid with methanol.

Preparation of $HRh(CO)(TPPTS)_3$

A. The ligand TPPTS (2.30g, 4.05 mmol) was added to hot water (40mL). To this $RhCl_3\cdot 3H_2O$ in water (2mL) was added. After 15 seconds formaldehyde (4mL, 27% in H_2O) immediately followed by KOH (0.35g, 6.24 mmol) in water (5mL) were added. A yellow solution formed almost immediately. The reaction solution was allowed to stir for 10 minutes and cool to room temperature. Water was evaporated under reduced pressure. The resultant yellow solid was taken up with minimal water and the yellow solid was precipitated with ethanol.

B. The ligand TPPTS (0.52g, 0.92 mmol) was added to water (10mL) and stirred under nitrogen until completely dissolved. $Rh(acac)(CO)_2$ (0.050g, 0.19 mmol) was added to the TPPTS solution. Upon complete dissolution an atmosphere of H_2/CO (1:1) was introduced and allowed to flow slowly for 18 hours. The yellow solution was filtered and evaporated to 1 ml. Ethanol was added to precipitate a dark yellow solid. The solid (I) was filtered, washed with hexanes, and dried under vacuum. Additional ethanol was added to the filtrate to precipitate additional solid (II). The mixture was centrifuged and (II) was dried in the vacuum oven. The liquid

was evaporated and the resultant solid (III) was dried under vacuum. Phosphorous nmr analysis determined that (I) was HRh(CO)(TPPTS)$_3$, the second precipitation (II) yielded a mixture of HRh(CO)(TPPTS)$_3$ (59%) and OTPPTS (41%). The solid (III) was OTPPTS.

In situ Preparation of the Supported Hydrophilic Film Catalyst

TPPTS (0.98g, 1.73 mol) is added to water (30 mL). To this Rh(acac)(CO)$_2$ (0.0098g, 3.72x10^{-5} mol) is added and stirred until completely dissolved. At this time an atmosphere of H$_2$/CO (1:1) is introduced and stirring is continued for 3 hours. This procedure produces HRh(CO)(TPPTS)$_3$, and excess TPPTS, as evidence by ^{31}P NMR. To the stirring solution the liquid polymer and/or high boiling liquid were added. Silica gel was then added in the amounts specified. The water is then evaporated under reduced pressure, and the resultant yellow solid is then placed under vacuum at 40°C overnight.

Catalytic Run

The catalyst (2.0g) and 1-hexene (50mL) are added to a 300 mL Parr pressure reactor. The reactor is sealed, flushed three times with argon (50psi), and allowed to stir for 30 minutes to check for leaks. If no leaks are evident, the argon is bled, the reactor is flushed three times with H$_2$/CO (1:1, 50psi), and heated to the reaction temperature. After 30 minutes at reaction temperature the reactor is filled to a final pressure of 83 psi. The reaction is then monitored by the uptake of H$_2$/CO gas. Table 4-2 is a compilation of the data presented in the results and discussion section.

Table 4-2. Activities for the Hydroformylation of Liquid substrates with SIIFC.

Film	substrate	solvent	mass of film (g)	% poly	[Rh]x10e6 (mol/g cat)	mass support (g)	P/Rh	delta	Activity (TON/min)	n/b
none	1-hexene	neat	0.00	0	7.90	4.08	43	0.20	1.27	10.30
PEG 600	1-hexene	neat	2.83	100	3.78	6.16	45	0.50	2.58	7.42
PEG/water	1-hexene	neat	5.70	50	3.60	4.08	45	1.40	8.31	6.50
PEG	1-hexene	neat	5.70	100	3.60	4.08	44	1.40	24.70	6.00
PEG 600	1-hexene	cyclohexa	5.70	100	3.60	4.08	44	1.40	0.19	2.00
PEG 600	1-hexene	1-hexene/ valeraldehyde	5.70	100	3.60	4.08	44	1.40	7.58	5.50
PEG 600	1-Octene	neat	5.70	100	3.60	4.08	44	1.40	2.47	5.00
PEG 600*	1-Octene	neat	5.70	100	3.60	4.08	44	1.40	20.02	5.36
PEG 600	1-Octadecene	neat	5.70	100	3.60	4.08	44	1.40	1.35	4.00
PEG600/ surfonyl 485	1-Octene	neat	5.70	80	3.60	4.08	44	1.40	4.59	5.09
PEG600/water	1-hexene	neat	5.70	0	3.60	4.08	44	1.40	15.60	15.60
PEG600/water	1-hexene	neat	5.70	25	3.60	4.08	44	1.40	1.18	25.50
PEG600/water	1-hexene	neat	5.70	49	3.60	4.08	44	1.40	7.93	5.32
PEG600/water	1-hexene	neat	5.70	75	3.60	4.08	44	1.40	15.61	6.50
PEG 600	1-hexene	neat	5.70	100	84.00	4.08	44	0.06	2.74	4.07
PEG 600	1-hexene	neat	5.70	100	29.50	4.08	44	0.18	18.57	6.30
PEG 600	1-hexene	neat	5.70	100	10.90	4.08	44	0.50	7.05	7.42
PEG 600	1-hexene	neat	5.70	100	7.70	4.08	44	0.70	9.96	6.50
PEG 600	1-hexene	neat	5.70	100	1.20	4.08	44	2.00	2.89	5.50

Table 4-2. Activities for the Hydroformylation of Liquid substrates with SHFC.

Film	substrate	solvent	mass of film (g)	% poly	[Rh]x10e6 (mol/g cat)	mass support (g)	P/Rh	delta	Activity (TON/min)	n/b
PEG 8000	1-hexene	neat	5.70	100	3.60	4.08	45	1.40	4.80	6.00
PEG 8000/water	1-hexene	neat	5.70	80	3.60	4.08	45	1.40	15.60	6.00
PVP	1-hexene	neat	5.70	100	3.60	4.08	45	1.40	0.44	7.24
PEO	1-hexene	neat	5.70	100	3.60	4.08	45	1.40	0.00	0.00
PVA	1-hexene	neat	5.70	100	3.60	4.08	45	1.40	0.00	0.00
Formamide	1-hexene	neat	5.70	100	3.60	4.08	44	1.40	0.63	17.00
Formamide	1-hexene	neat	5.70	100	3.60	4.08	44	0.05	1.19	9.20
Formamide	1-hexene	neat	5.70	100	3.60	4.08	44	0.70	0.67	9.20
Formamide	1-hexene	neat	5.70	100	3.60	4.08	44	1.40	0.58	12.40
PEG 600/ formamide	1-hexene	neat	5.70	50	3.60	4.08	44	1.40	2.81	9.36
Glycerol	1-hexene	neat	5.70	100	3.60	4.08	44	1.40	0.03	21.70
homogeneous	1-hexene	neat	0.00	0	3.68	0.00	44	0.00	68.00	3.00
biphasic	1-hexene	40/10a	0.00	0	3.68	0.00	44	0.00	0.00	35.90

Conditions: Temperature 100C; Pressure 50 psig (1:1 Hydrogen/carbon monoxide)

* reaction was run at 125 C.

a 50 ml. 1-hexene and 10 ml. water.

PEG - polyethylene glycol

PVP - polyvinylpyrrolidinone

Results and Discussion

Statement of the Problem

In the previous chapter we addressed the problem of the hydroformylation of gaseous substrates using supported thin film catalysts. In this chapter we are going to expand this idea to include the realm of liquid substrates. This allows the hydroformylation of higher olefins by heterogenous catalysts. Currently, higher olefins can not be hydroformylated by vapor phase catalysis because the boiling points of the product aldehydes exceeds the optimal temperatures for rhodium based catalysts. For the same reason, an extra extraction (purification) step is required for homogeneous catalytic processes. Most homogeneous processes rely upon the distillation of the aldehydes from the reaction mixture for product separation. The goal of this project is to develop a heterogenous catalyst, using polymer films or high boiling liquids, for the hydroformylation of liquid substrates in batch reactors.

The heterogeneous catalytic system described herein consists of a catalytic hydrophilic film that covers a porous inorganic oxide. It is the boundary between the hydrophilic film and hydrophobic solution that prevents the leaching of the transition metal catalyst into the substrate solution.

Choice of Catalyst, Ligand and Film

Catalyst. We have chosen the phosphine modified rhodium complex $HRh(CO)(TPPTS)_3$ as our catalyst. This complex has high activity in biphasic systems

for the hydroformylation of ethylene and propylene.[95] It is also water soluble and insoluble in organic solvents. This insolubility should lead to a catalyst that does not leach into the reaction solution and remains in the hydrophilic film.

Synthesis of the complex has been done by two methods. The first was a directly analogous reaction to the synthesis of $HRh(CO)(PPh_3)_3$.[57] The synthesis is described in the experimental section of this chapter. This method yielded a pure complex as evidenced by ^{31}P nmr and infrared spectroscopy but in very low yields, less than 5% (see Figure 4-6).

The second method is by the simple ligand substitution of the acetylacetonate (acac) ligands on $Rh(acac)(CO)_2$ with TPPTS in the presence of carbon monoxide and hydrogen. Work up of the reaction solution decomposed most of the rhodium complex to an unidentified material. Phosphorous nmr of the reaction solution showed that the only product was $HRh(CO)(TPPTS)_3$ (see Figure 4-7). Purification of the reaction mixture decomposed much of the desired rhodium complex. It was determined that work up of the complex was not necessary and that the solution should be used without any further workup.

Ligand. The synthesis of TPPTS is not trivial. TPPTS readily oxidizes to OTPPTS. Phosphorous nmr, Figure 4-8, shows a single (singlet) resonance at -5.50 ppm. This complex is freely soluble in water and slightly soluble in methanol. It is insoluble in ethanol, isopropanol, and most common organic solvents, such as acetone, chloroform, methylene chloride, benzene, toluene, and hexane. This insolubility makes TPPTS an excellent candidate as a rhodium ligand.
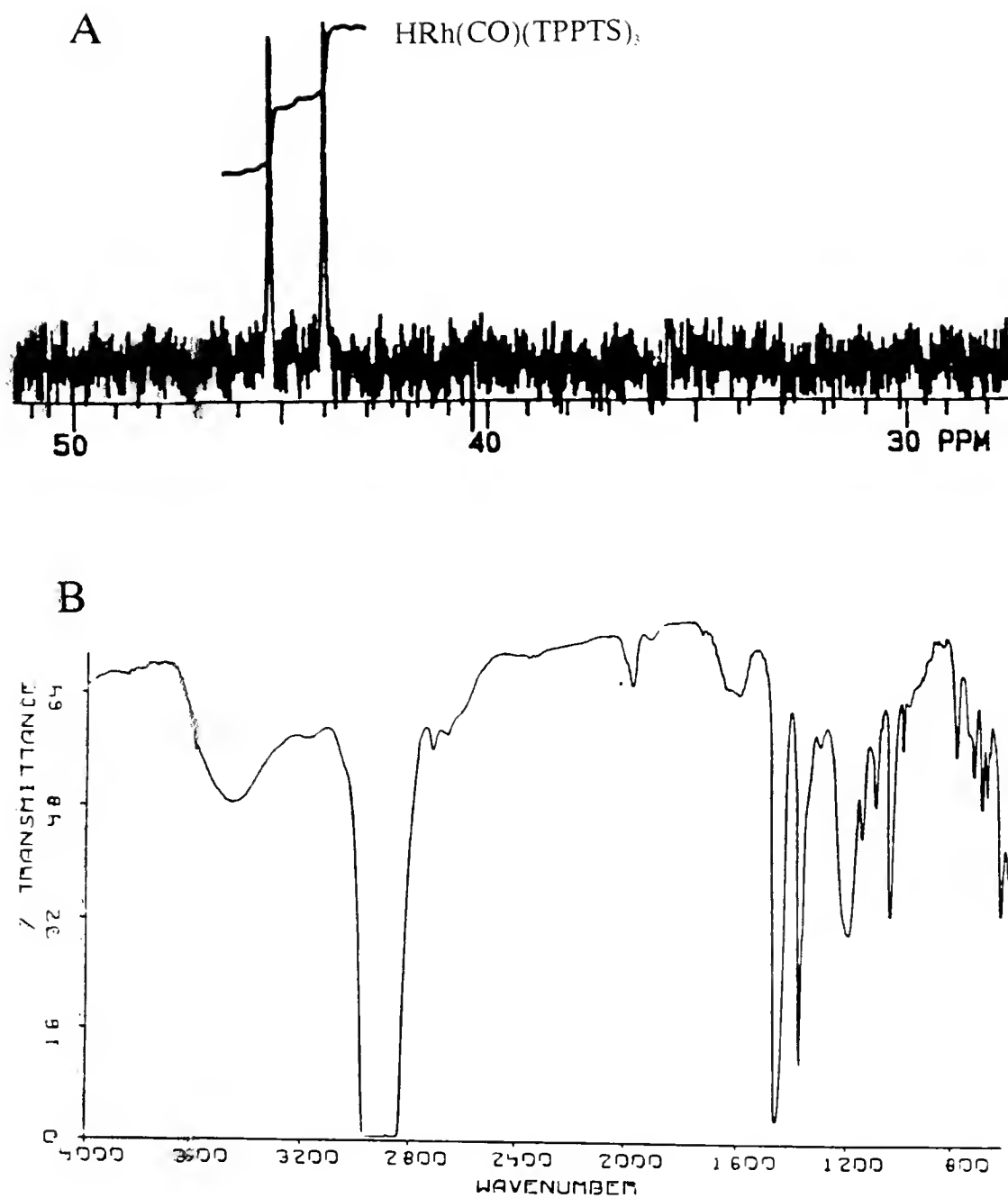
Figure 4-6.   Phosphorous nmr (A) and ir (B) of HRh(CO)(TPPTS)₃.
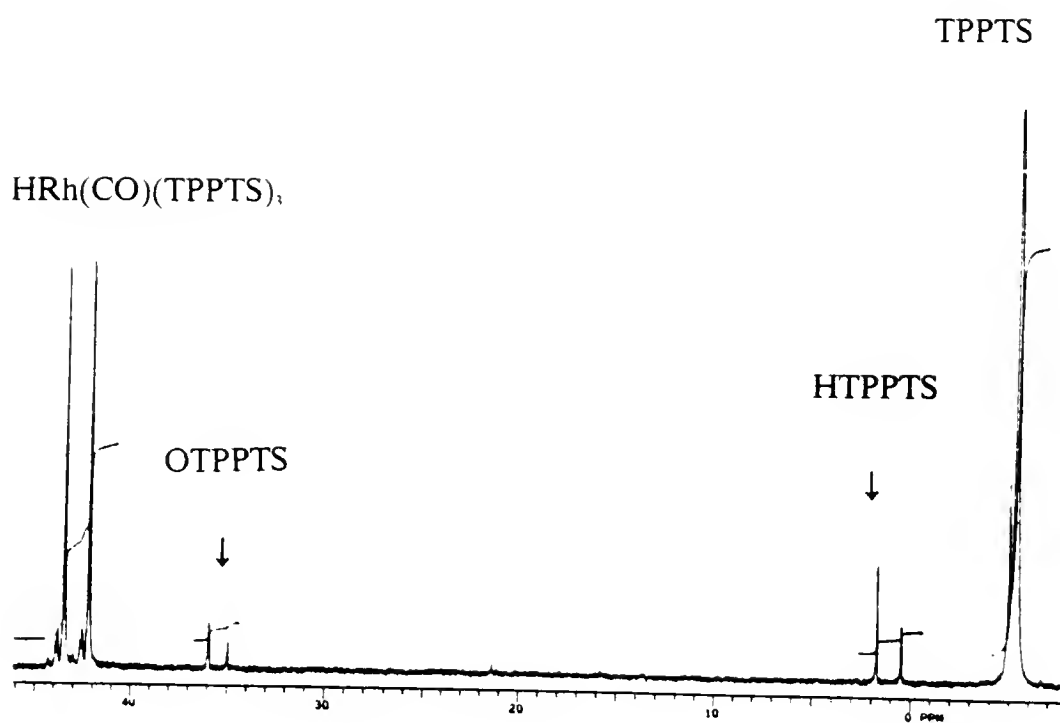
Figure 4-7. ^{31}P nmr spectrum of *in situ* generated HRh(CO)(TPPTS)$_3$.
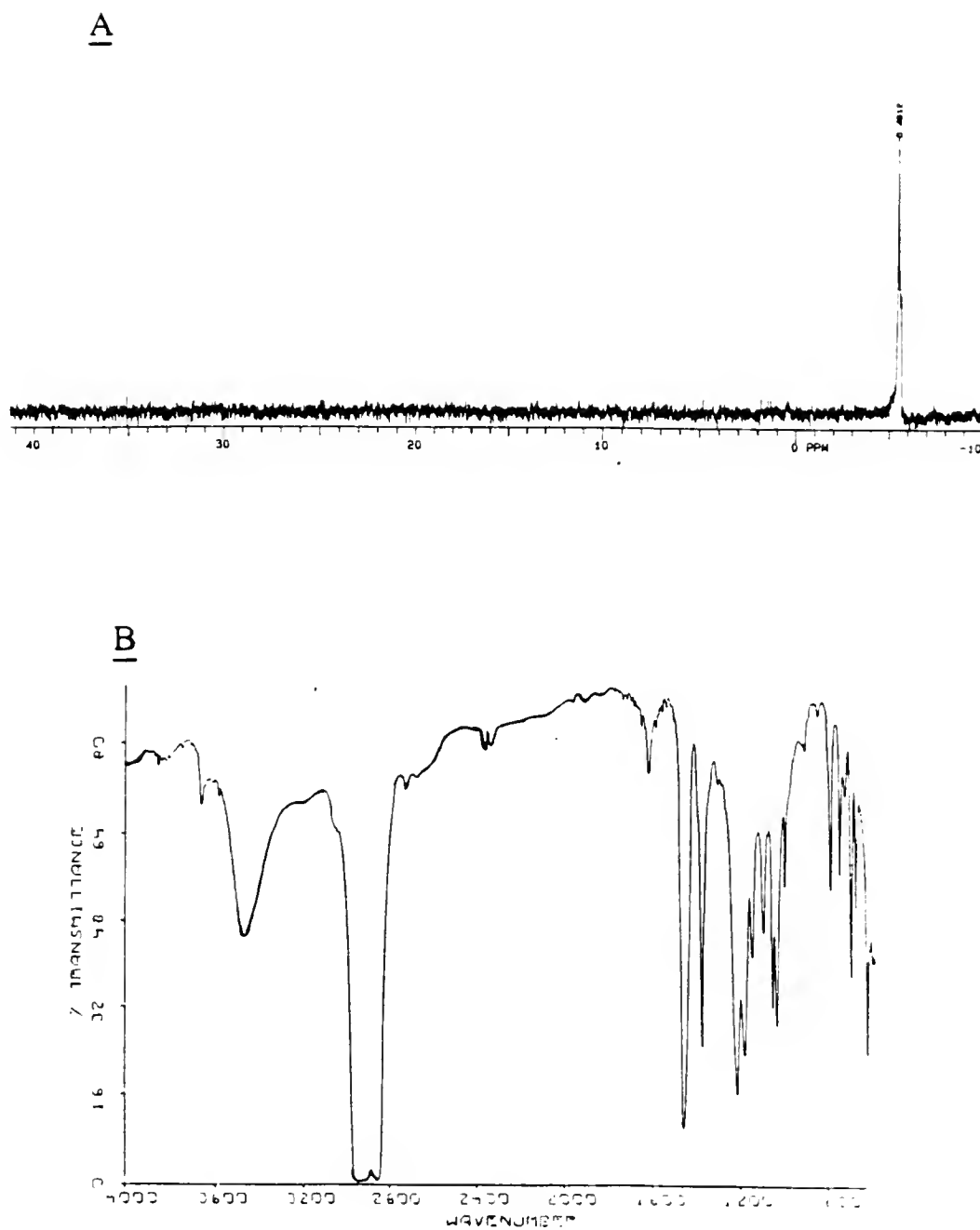
<u>A</u>

<u>B</u>

Figure 4-8.   Phosphorous nmr (A) and ir (B) of TPPTS.

Film. An ideal liquid phase for SPLC's would be a non-volatile, film forming liquid that can solubilize active rhodium catalysts. In order to hydroformylate liquid substrates the film must also be insoluble in organic solvents. Hydrophilic polymers possess most of these criterion making them excellent candidates as films. The main focus of this work will concentrate on polyethyleneglycol (PEG) as the liquid phase. Polyethylene glycol 600 is a liquid at low molecular weights and solubilizes the rhodium complex $HRh(CO)(TPPTS)_3$. Polyvinyl alcohol, polyethylene oxide and polyvinylpyrolidinone were also used. In addition to polymers, the high boiling liquids formamide and glycerol were examined as films.

Calculations

Activity

The activities were calculated by the method of initial rates because the pressure of reactant gases over the catalyst changes as the reaction proceeds this continually changes the reaction conditions. Gas uptake or consumption was followed for at least the first 15 psig of the reaction. Plots of the change in pressure, P, versus time, t, produced a curve (see Figure 4-9). The slope of the tangent to the curve at t=0 leads to the initial activity of the catalyst. From the slope, m, the time required for a specified amount of gas uptake can be calculated. 6 psig was used for this amount (6 psi was chosen because it is early enough in to reaction so as the conditions have not changed considerably from the initial conditions).
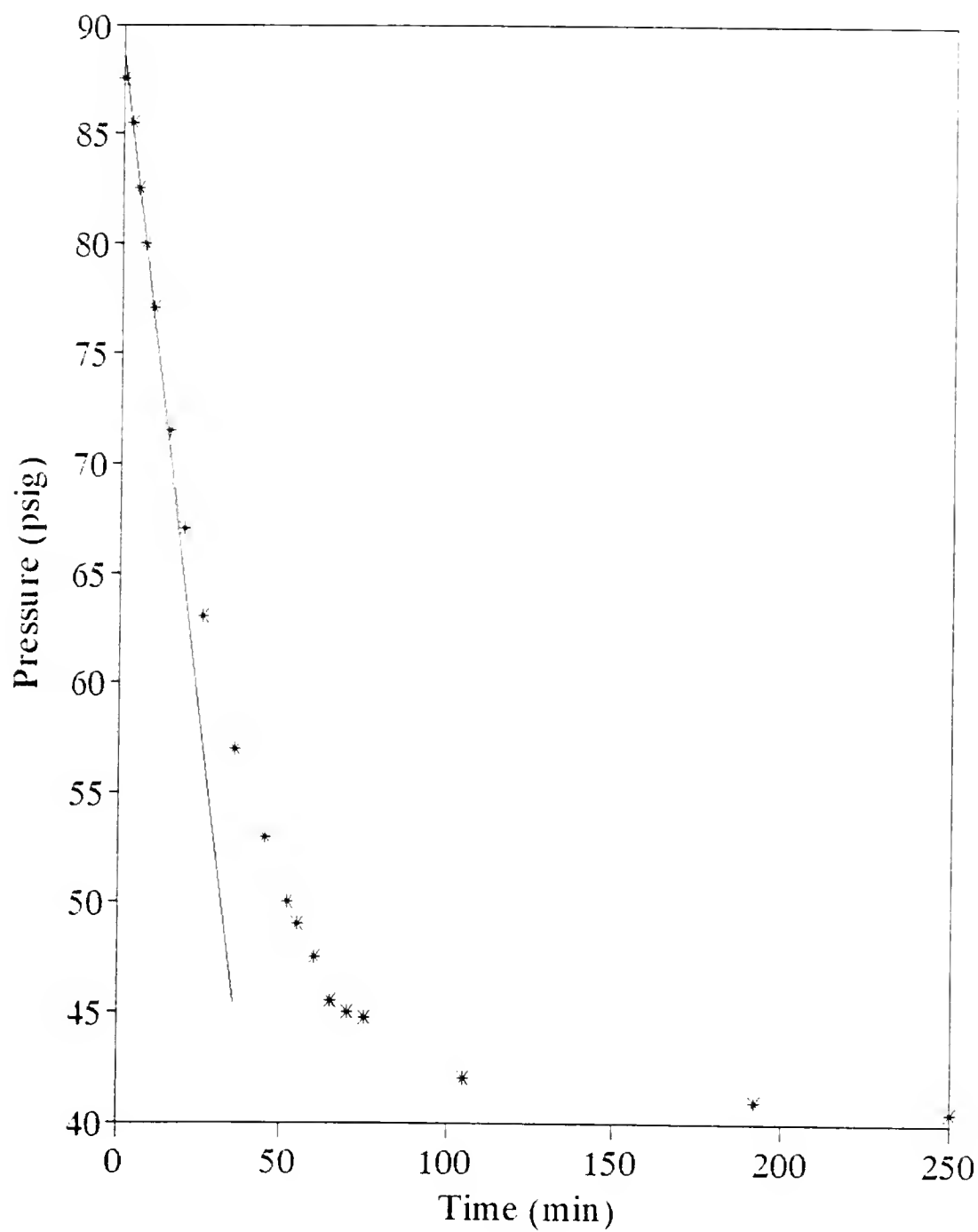
Figure 4-9.   Change in total pressure in a batch reator with reaction time.

$$t_R = \frac{P_R - P_o}{m} \qquad \text{(equation 4.1)}$$

The number of moles of H_2 used in 6 psig of reactant gas can also be calculated. For every one mole H_2 consumed one mole of aldehyde is produced. Dividing the number of moles of products (n_p) by the moles of rhodium catalyst (n_c) yields the turnover number (TON).

$$TON = \frac{n_p}{n_c} \qquad \text{(equation 4.2)}$$

Dividing TON by the time required to take up 6 psi of syn gas gives the activity in TON/min.

$$a = \frac{TON}{t_R} \qquad \text{(equation 4.3)}$$

Selectivity

Selectivity was calculated by the ratio of product peaks obtained via gas chromatography and were verified by ^1H nmr. The ratio of the calibration corrected integrations for the linear and branched aldehydes gave the n/b ratios for a given reaction. Proton nmr integration ratios of the aldehyde protons also gave the n/b ratios.

Calculation of δ

The amount of pore volume filled, δ, can be easily calculated. Equation 4.4 shows that δ is the ratio of the volume of the film (V_f) to the pore volume (V_s) of the support. The density of the PEG film was approximated to be 1.12 g mL^{-1}. Figure 4-10 depicts the amount degree of pore filling when δ > 1 and δ < 1.

$$\delta = \frac{V_f}{V_s}$$
(equation 4.4)

Hydroformylation of Olefins with Supported Hydrophilic Catalysts

The catalyst described consists of a water soluble/organic insoluble catalytic polymer film supported on silica gel. Polyethylene glycol 600 was chosen for study because of it is hydrophilic and liquid properties at reaction temperatures. We have investigated and optimized the activity of several of these catalysts by studying the effects of pore filling and the addition of water to the film. All of the catalysts studied showed considerable activity for hydroformylation of 1-hexene.

In addition to PEG, several other polymers and high boiling liquids were tested for hydroformylation activity and will be discussed *vide infra*. The substrates 1-hexene, 1-octene, and 1-octadecene were studied.
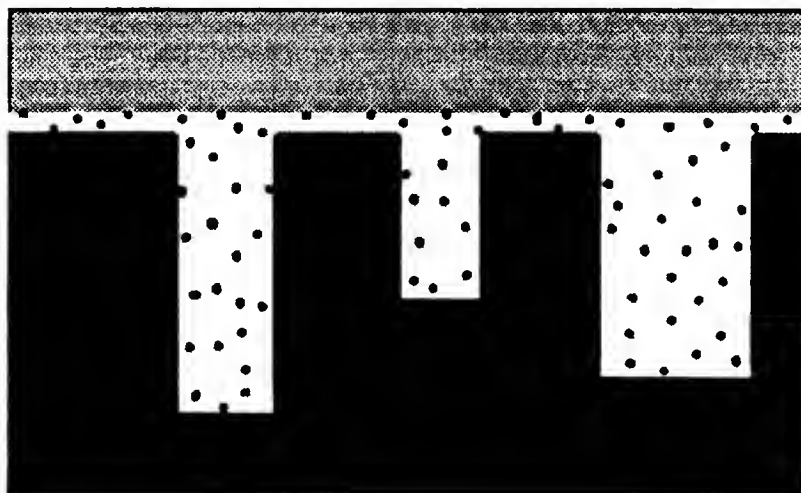
A

Reaction Solution
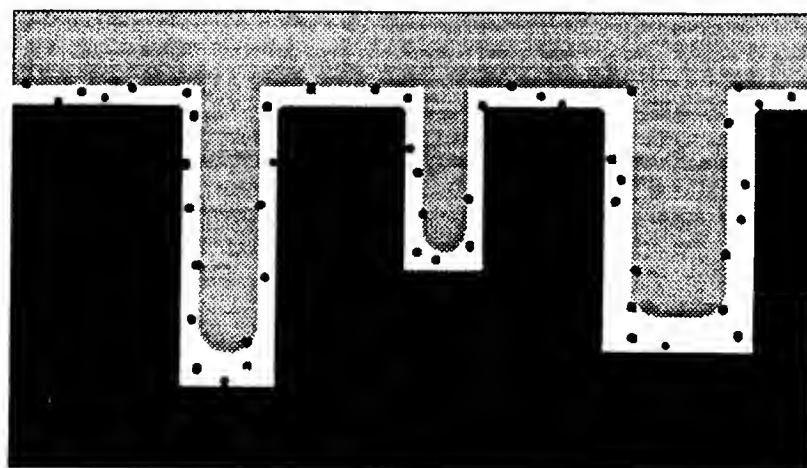
Liquid Phase

Support

B

Reaction Solution

Liquid Phase

Support

Figure 4-10.   Illustration demonstrating pore filling on the surface of a support.
A. The degree of pore filling (δ) is less than 1.0. B. The degree of
pore filling is greater than 1.0.

Control experiments were run to test the activity of the catalyst with the individual components of the film, e.g., PEG and water. A catalyst that contained no film was run at 100°C and 90 psig total pressure. The activity was 1.27 TON/min. A PEG film catalyst with a δ of 0.50 increased the activity two fold (2.58 TON/min), while the selectivities remained unchanged. A similar catalyst was prepared but water was added to "loosen" the film. The resultant catalyst had a δ of 1.40 and the film was 50% PEG and 50% water. The activity of this catalyst was 8.31 TON/min. Figure 4-11 shows the activity curves of these catalysts. The addition of a film increases the activity of the system. One explanation for this is that the film fills the pores of the surface and creates a homogeneous catalytic system. Since the pressure is constantly changing over the reaction solution no direct comparison could be made between a reported homogeneous catalyst and our supported thin film catalyst. We decided to determine the activities of a homogenous catalyst, $HRh(CO)(PPh_3)_3$ and excess phosphine, in our setup and under our conditions. Hydroformylation of 1-hexene using the homogeneous catalyst showed an activity of 68 TON/min and a n/b ratio of 3:1.

Comparing PEG to other systems

The most active supported polymer system to date was the catalyst containing polyethylene glycol (MW=600), $HRh(CO)(TPPTS)_3$ and excess TPPTS supported on silica gel. This system showed an activity of 24.7 TON/min and a n/b ratio of 6:1 at 100°C and 85 psig. Our system showed an activity which was roughly three times
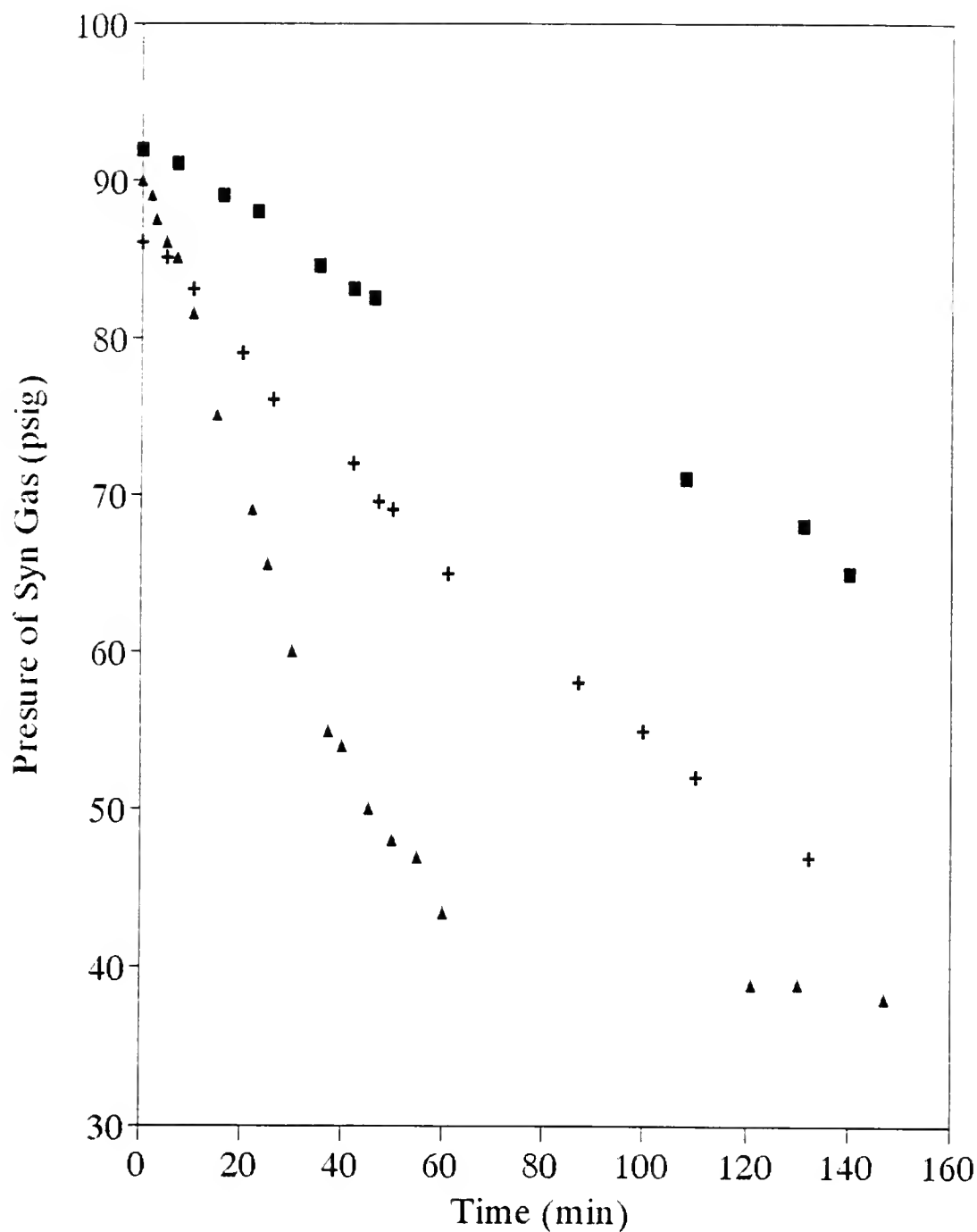
Figure 4-11. Gas uptake measurements for the hydroformylation of 1-hexene with SHFC. ■ - no film; + - PEG film ($\delta = 0.80$); ▲ - PEG and H_2O film ($\delta = 1.40$). Rhodium source - $HRh(CO)(TPPTS)_3$; P/Rh 44:1: Support - silica gel.

smaller than our homogeneous catalyst system. These results are encouraging because the activities of the supported catalysts were expected to be several orders of magnitude lower than that of the homogeneous catalysts.

Comparisons to the biphasic catalyst system ($HRh(CO)(TPPTS)_3$ and excess TPPTS in water and 1-hexene, at 100°C and 85 psig) yielded a promising result. This catalyst showed an activity of 0.085 TON/min and a selectivity of 35:1 (see Table 4-3). Inefficient mixing of the aqueous and organic layers probably contributed to the low activity of the catalyst. This experiment demonstrates the effectiveness of supported thin film catalysts relative to the biphasic system.

Solvent effects

Homogeneous hydroformylation systems using rhodium catalysts require an inert solvent. It is known that the activity of the homogenous rhodium systems reach a maximum at a specific concentration of the substrate, above this point the activity drops dramatically.[*] If the catalyst film is acting as a homogeneous film, the polymer or liquid phase will act as the solvent (1-hexene has low solubility in PEG) and the need for an external solvent, such as cyclohexane or toluene, would be eliminated.

Both the activity and selectivity of the PEG catalyst ($\delta = 1.40$) in cyclohexane were dramatically lower than in neat 1-hexene (see Table 4-4). Therefore it follows that an external solvent only hinders the activity of the catalyst due to mass transfer of the substrate to the film interface. It should be mentioned that some activity was probably occurring at the solvent/polymer interface.

Table 4-3.   Comparisons of Supported Catalyst with Homogeneous
and Biphasic Catalysts.

Catalyst	Activity (TON/min)	n/b
HRh(CO)(TPPTS)$_3$/TPPTS/ PEG/silica[a]	24.7	6
HRh(CO)(TPP)$_3$ Homogeneous	68.0	3
HRh(CO)(TPPTS)$_3$/H$_2$O Biphasic	0.085	35

[a]-δ = 1.40.
Condtions: 100°C, 50 psig (1:1 H$_2$/CO)

Table 4-4. Activity of Catalysts in Various Solvent Systems.

Solvent	Activity (TON/min)	n/b Ratio
Cyclohexane[a]	0.19	2.00
1-Hexene[a]	24.70	6.02
Biphasic[b]	0.12	6.00

[a]Catalyst: $HRh(CO)(TPPTS)_3$/TPPTS/PEG 600/Silica
[b]Catalyst: $HRh(CO)(TPPTS)_3$ in H_2O and 1-hexene.
Conditions: 100°C, 50 psig syn gas.

Toluene was also used as a solvent. Toluene extracted the liquid polymer film form the support into solution leaving a silica supported rhodium catalyst. The activity of this system was low.

Presence of aldehydes

Although we have effectively eliminated the need for an inert solvent, the production of aldehydes as reaction proceeds will influence the nature of the solution. Commercial processes are concerned with how the catalyst will perform in an environment which is predominately aldehydes. In this case the reaction solution is more polar than in neat 1-hexene and may influence the activity and selectivity of the catalyst. The presence of aldehydes may compromise the biphasic nature of the system by the extraction of the polymer film into solution.

We tested the activity of some of our catalysts in a co-solvent reaction solution consisting of valeraldehyde and 1-hexene (1:1). This solvent system will simulate the presence of large amounts of aldehyde products, while allowing easy monitoring of the products by gas chromatography.

The PEG catalyst, with a δ of 1.4, showed an activity of 7.58 TON/min and a selectivity of 5.5:1 in the valeraldehyde/1-hexene co-solvent system. The drop in activity is expected due to the decrease in the concentration of substrate in solution. The ^{1}H nmr spectrum of the reaction solution showed the extraction of some of the polyethylene glycol into the reaction solvent mixture, but there was no evidence of phosphines (see Figure 4-12).
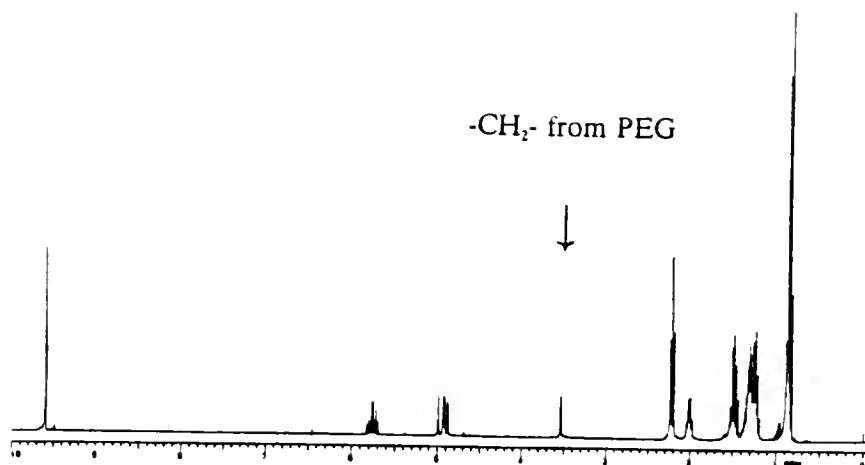
Figure 4-12. Proton nmr of the reaction solution after hydroformylation in 50/50 valeraldehyde/1-hexene.

Attempts to find a film that would not extract into an aldehyde solution were made by using the polymer film on silica which is refluxed 18 hours in valeraldehyde/1-hexene. Proton nmr of the aldehyde solution was taken to analyze for the extraction of the polymer. Two models of the polyethyleneglycol catalysts with δ's of 0.50 and 1.40 were tested for leaching of the polymer film from the support. Extraction of some of the polymer into the solution occurred in both cases. Figure 4-13 shows the ^{1}H nmr of the reaction solution after 18 hours in the presence of the supported film. A high molecular weight PEG (MW=8,000) polymer model showed no signs of elution of the film into the valeraldehyde/1-hexene solution (see Figure 4-14). Other polymers that were also tested were polyvinylpyrolidinone, polyethylene oxide and polyvinyl alcohol. All showed no leaching into the reaction solvent. However, hydroformylation of 1-hexene with catalysts having these films showed low activities, *vide infra*.

Altering the polarity and composition of the PEG film was accomplished by addition of water, sodium sulfate or sodium nitrate to the polymer phase. All of these models showed extraction of the polymer film into solution but not all to the same degree. The sodium sulfate modified film was less extractable than a film of PEG alone, while the sodium nitrate film showed considerable leaching of the PEG (see Figure 4-15).
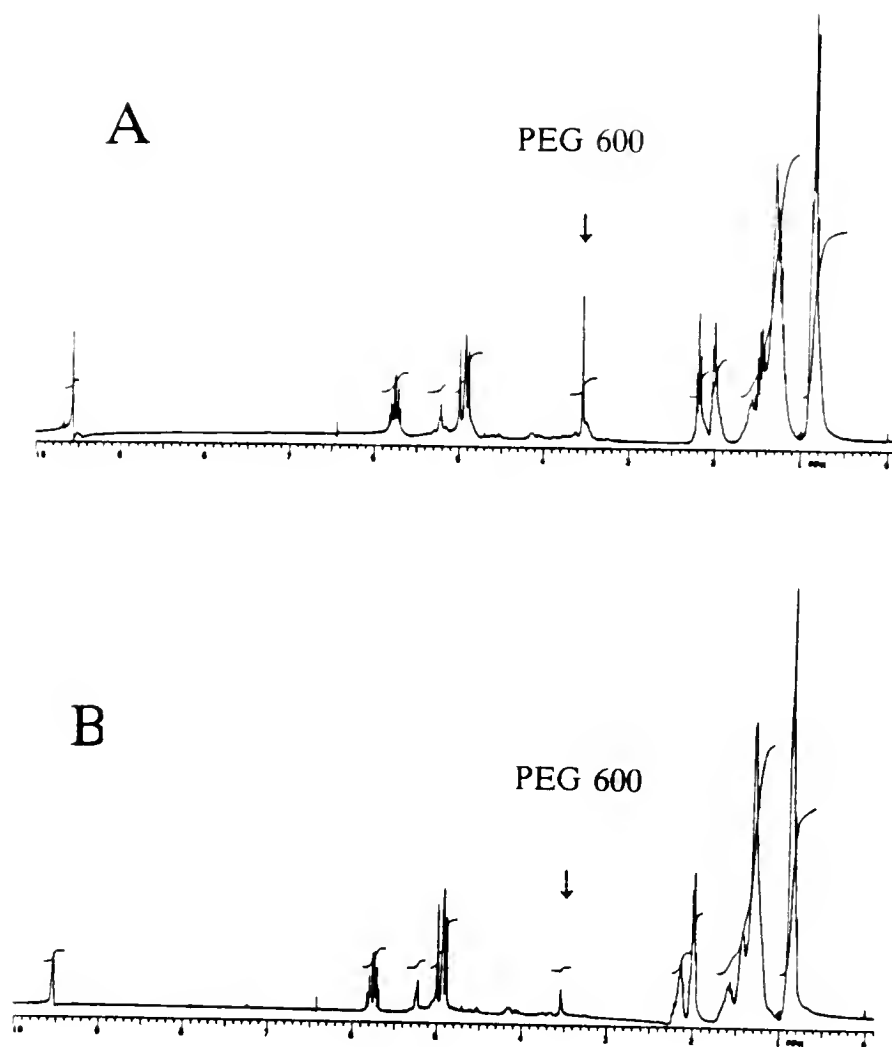
Figure 4-13. ¹H nmr of 50/50 valeraldehyde/1-hexene after 18 hours refluxed and stirring with silica coated with PEG 600. Spectrum A is a model with a δ of 1.40. Spectrum B is a model with a δ of 0.50.
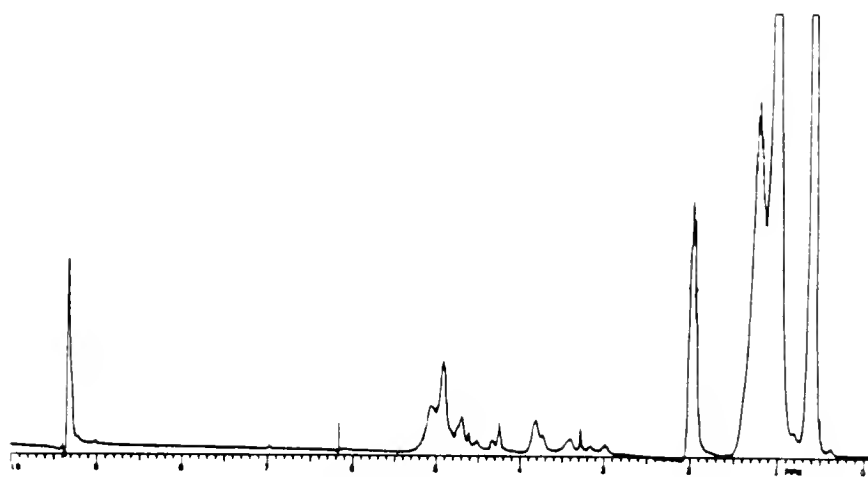
Figure 4-14. ^{1}H nmr of 50/50 valeraldehyde/1-hexene after 18 hours refluxed and stirring with silica coated with a high molecular weight PEG.
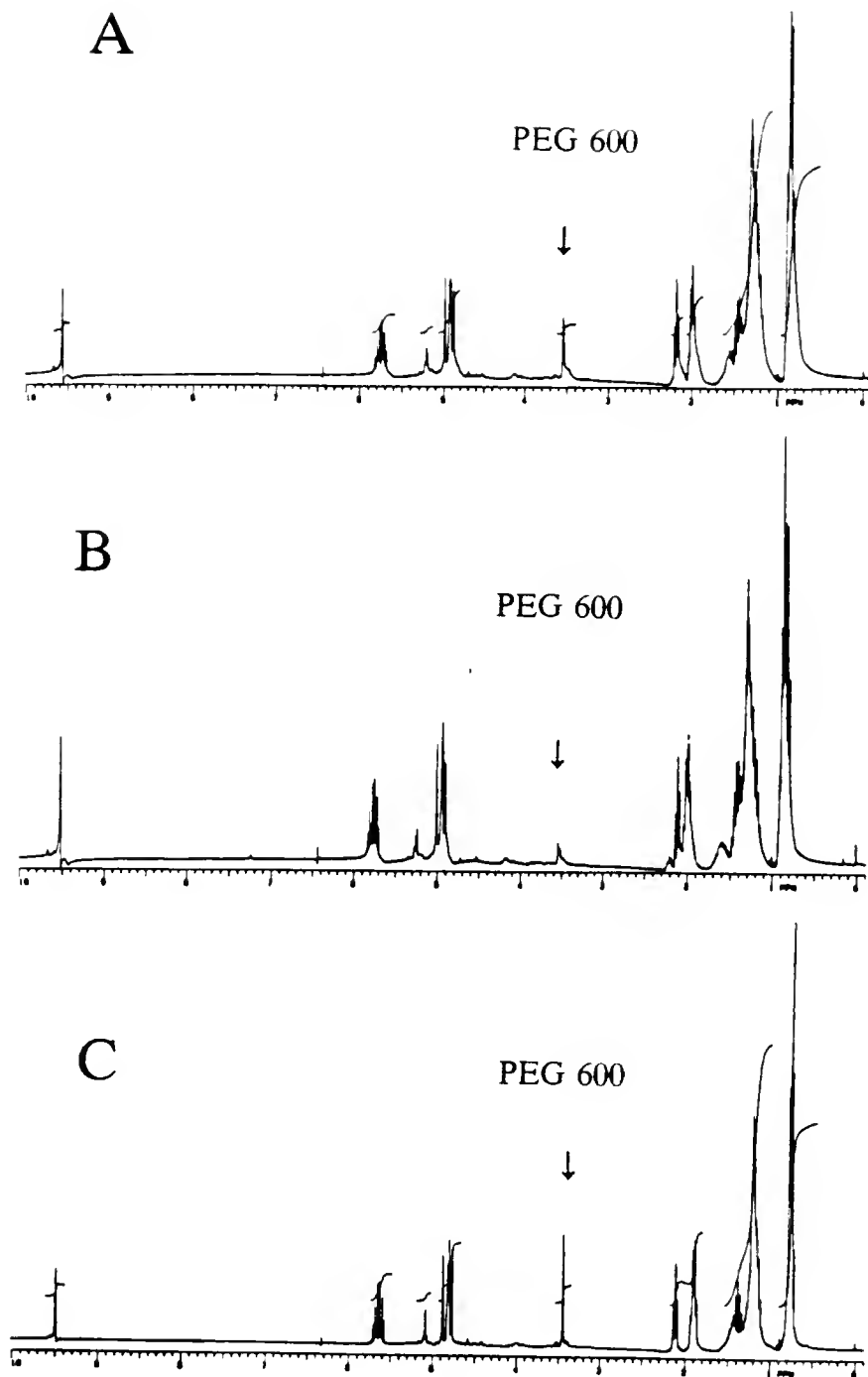
Figure 4-15. Proton nmr spectra of 50/50 valeraldehyde/1-hexene solutions after 18 hours refluxed and stirring with silica coated with PEG and additives. Spectrum A The film consists of PEG and H_2O. Spectrum B the film consists of PEG and $Na_2SO_{4(aq)}$. Spectrum C the film consists of PEG and $NaNO_{3(aq)}$.

Isomerization of 1-hexene to 2-hexene

The production of undesirable side products by the catalyst are of interest, particularly the isomerization of α-olefins to internal olefins. The formation of internal olefins needs to be limited for the following reasons. First, the hydroformylation of internal olefins is much slower than α-olefins, thus reducing the overall activity of the catalyst. Second, the products derived from the internal olefin are branched aldehydes which are economically inferior to the linear products and third the separation of internal and α-olefin is difficult. We have tested for the formation of 2-hexene with the PEG catalyst ($\delta = 1.4$) and found the isomerization to be minimal, a selectivity of 94.8% aldehydes was observed. In the presence of valeraldehyde (heptaldehyde simulant) the isomerization rate increases and the selectivity to aldehydes drops to 86.2%. No change in the n/b ratio was observed.

Test for leaching

Throughout this chapter we have been concerned with the elution of the polymer film into solution. However, a more important consideration is the leaching of the costly rhodium catalyst from the film into the reaction solution. The catalytic systems presented herein uses a hydrophilic polymer and water soluble phosphine modified rhodium catalysts. The biphasic nature between the polymer and the substrate solution prohibits the rhodium from leaching.

Requirements for the polymer films are that they solubilize the rhodium phosphine complexes and form a biphasic system in organic solvents (e.g., 1-hexene

or cyclohexane). One method to test for leaching of the catalyst into solution is to test the reaction solution for activity. Filtration of the catalyst and further testing of the 1-hexene reaction solution for activity showed no further gas uptake over 18 hours. Homogeneous rhodium catalysts are extremely active and even the presence of ppm levels of the catalyst would result in some gas uptake over this period.[13] In addition ^{31}P and ^{1}H nmr of the solution showed no resonances suggesting the absence of any phosphine or rhodium phosphine species in solution. Proton nmr showed no signals for PEG or aromatics, also signaling the lack of phosphines (see Figure 4-16).

Characterization

Phosphorous NMR of the catalysts. Test for the solubility of the rhodium complex and sulfonated phosphine in the film and on the silica support were followed by ^{31}P nmr. Nuclear magnetic resonance spectra were taken both in the presence and absence of co-solvents (e.g. 1-hexene or cyclohexane). Both methods yielded similar spectra. Supported catalysts with a liquid film of PEG 600 showed a broad resonance at -3 ppm and was assigned to TPPTS. The ^{31}P nmr spectrum of this catalyst after hydroformylation shows the presence of both TPPTS and OTPPTS (29 ppm), see Figure 4-17. This signifies the oxidation of the excess phosphine ligand during hydroformylation. The broadening can be attributed to t_2 relaxation due to the presence of solids (silica gel). The absence of a Rh-P signal can be attributed to the low concentration of Rh in the film. To verify the signals in the nmr, TPPTS in PEG gave a signal at -5 ppm. Also a supported film with OTPPTS in PEG was prepared and the ^{31}P nmr showed a resonance at 29 ppm (see Figure 4-18).
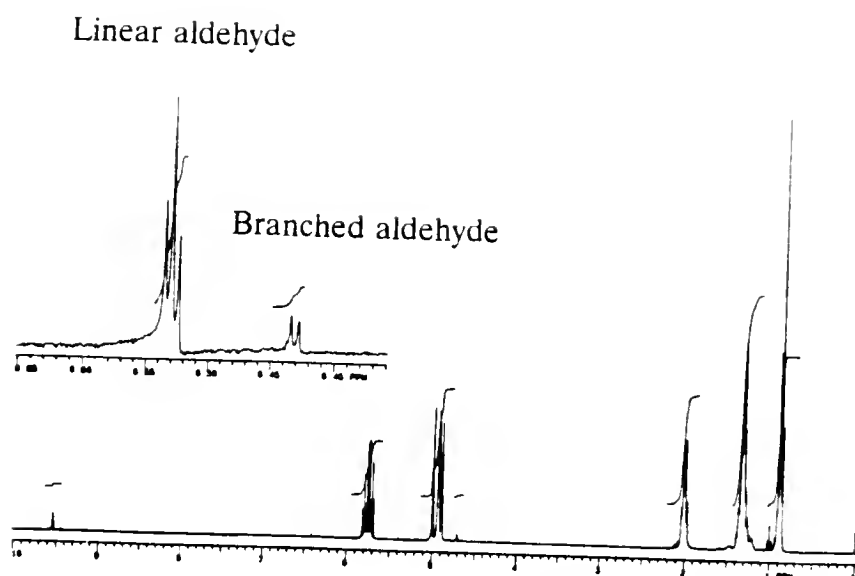
Linear aldehyde

Branched aldehyde

Figure 4-16. ¹H nmr of the reaction mixture after hydroformylation of 1-hexene.
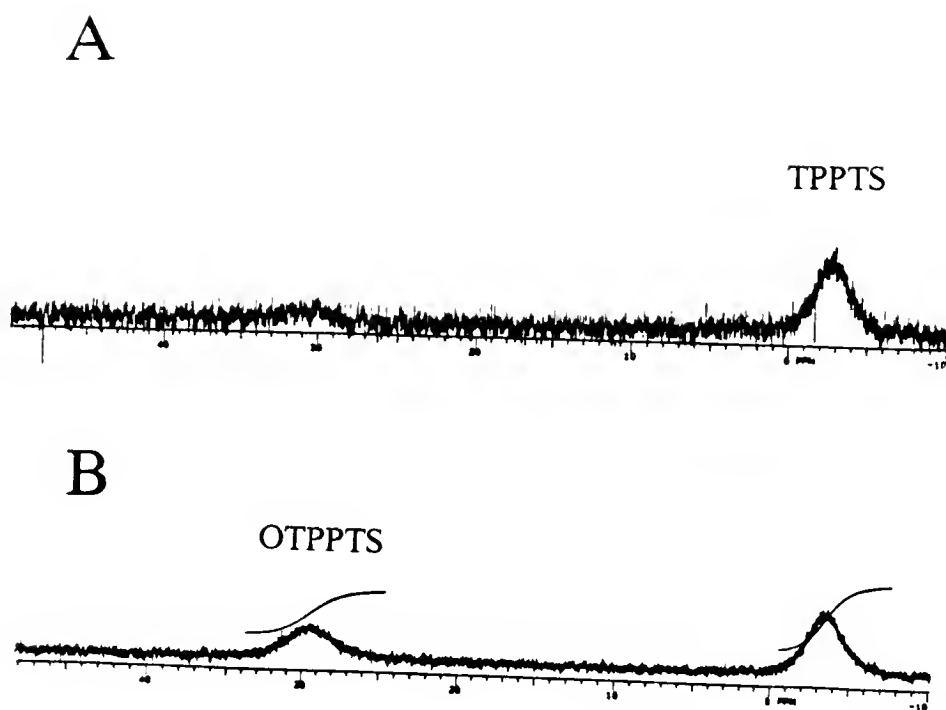
Figure 4-17. ^{31}P nmr of the solid HRh(CO)(TPPTS)$_3$/TPPTS/PEG/Silica gel catalyst. Spectrum A before reaction. Spectrum B after reaction. This spectra was taken as if it were a liquid sample.
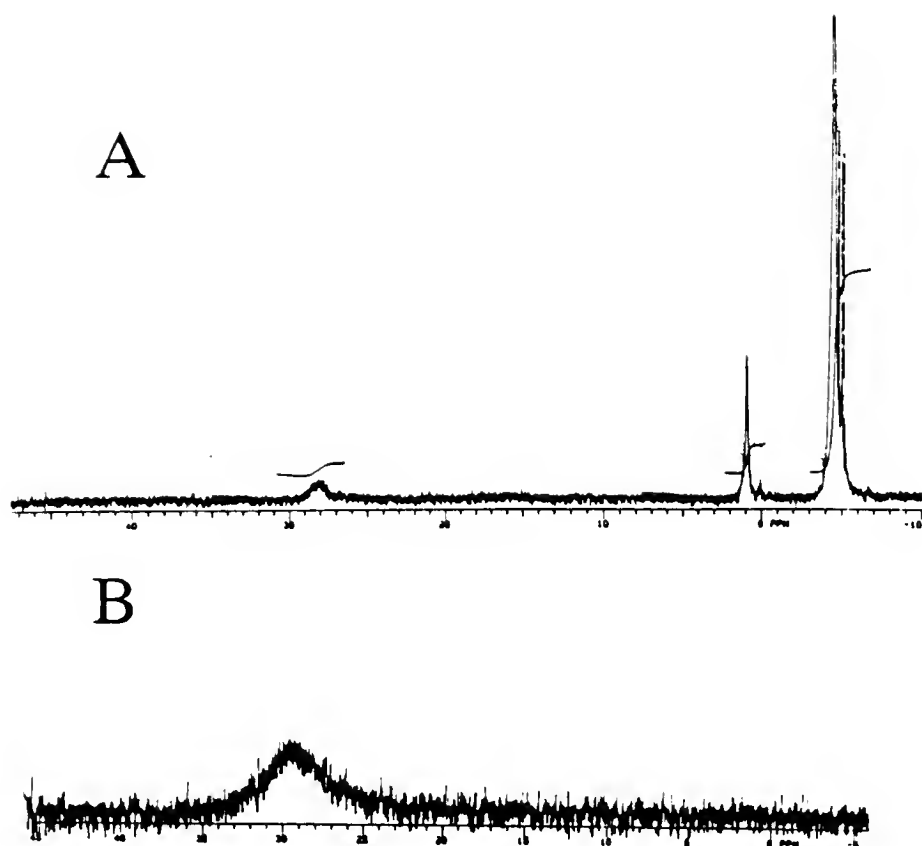
Figure 4-18. ^{31}P nmr spectra of phosphines in PEG. Spectrum A TPPTS in liquid PEG. Spectrum B Silica gel coated with OTPPTS in a PEG film.

The nmr spectra of catalysts that do not have liquid polymer and/or water films do not show resonances. Similarly a catalyst with polyethylene glycol 8000, a solid film at room temperature, as the polymer film also shows no resonances in the ^{31}P nmr spectrum. The conclusion is that catalysts with liquid films have the catalyst dissolved in solution and the mobility of the phosphines produces a solution nmr. The rhodium complexes in a solid matrix has no mobility and interactions with the substrate would be limited to the complexes at the liquid/solid interface.

Proton nmr of the supported catalyst. The ^{1}H nmr spectrum of the PEG catalyst on silica showed very broad indistinguishable peaks. The catalyst prior to hydroformylation was washed with D$_2$O (see Figure 4-19). The ^{1}H nmr spectrum of the wash showed the presence of PEG and TPPTS. After the hydroformylation reaction the catalyst was dried and washed with D$_2$O. The ^{1}H nmr also showed the presence of PEG. This coupled with the lack of the PEG resonance in the ^{1}H nmr of the reaction solution demonstrates that the film remained intact throughout the hydroformylation experiment. Resonances in the aromatic region revealed that the phosphine also remained in the film. Lastly, a resonance at 9.4 ppm shows that some product aldehyde remains incorporated in the film. It was observed in the hydroformylation of 1-octene that the rate of reaction increased with the reaction time, *vide infra*. The retention of some product aldehyde in the film suggests that the aldehyde contributes to the general make up of the film and acts as a surfactant. This may be causing the increase in the reaction rate with time.
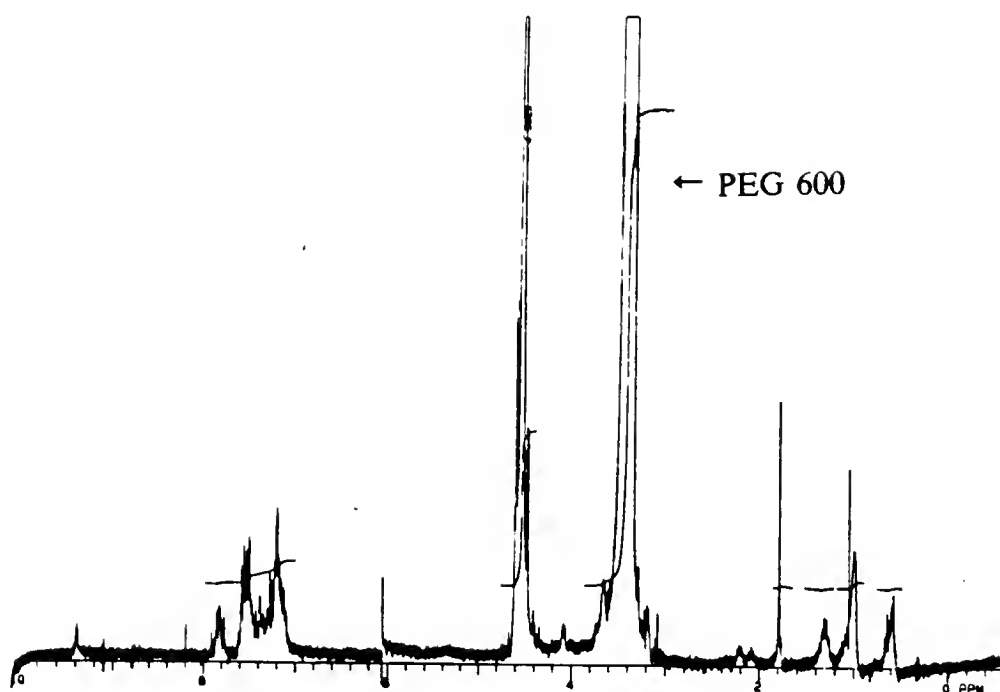
Figure 4-19. Proton nmr of the catalyst film after reaction, film was washed from the support with D₂O.

Higher olefin substrates

If the film covering the support is homogeneous, the activity of the catalyst for different substrates relies upon the limited solubility of that substrate in the polymer film. It has been shown that the activity of supported aqueous phase catalysts does not change with the change in substrate indicating that the active portion of the catalyst lies at the organic/aqueous interface[92,94]. We have studied the hydroformylation of higher olefins such as 1-octene and 1-octadecene with the PEG catalyst ($\delta = 1.40$) at 50 psig of syn gas and 100°C. Table 4-5 shows the activity and selectivities of these substrates. The trend is that as the chain length of the substrate gets larger the activity of the catalyst decreases. This demonstrates the dependance on the solubility of the substrate in the polymer film, and supports the theory that hydroformylation occurs in a homogeneous liquid solution on the support surface.

Curiously, as the reaction proceeded, a considerable increase in the initial rate of the reaction occurred for the PEG film catalyst. During the hydroformylation of 1-octene, the activity at the early stages of the reaction was 2.47 TON/min, but two hours later the rate had increased to 5.05 TON/min (see Figure 4-20). This increase could be due to the retention of product aldehyde in the film. The aldehyde then acts as a surfactant and allows a higher solubility of 1-octene in the film, thus increasing the activity. As described *vide supra* the ^{1}H nmr spectrum of the washed film from the 1-hexene hydroformylation reveals the presence of aldehydes in the film.

Table 4-5.   Hydroformylation of various substrates.

Substrate	Activity (TON/min)	n/b Ratio
1-Hexene	24.7	6
1-Octene	2.47	5
1-Octadecene	1.35	4

Catalyst: Rhodium source: HRh(CO)(TPPTS)$_3$; Phosphine: TPPTS; Polymer: PEG 600; Support: Silica; $\delta = 1.40$.

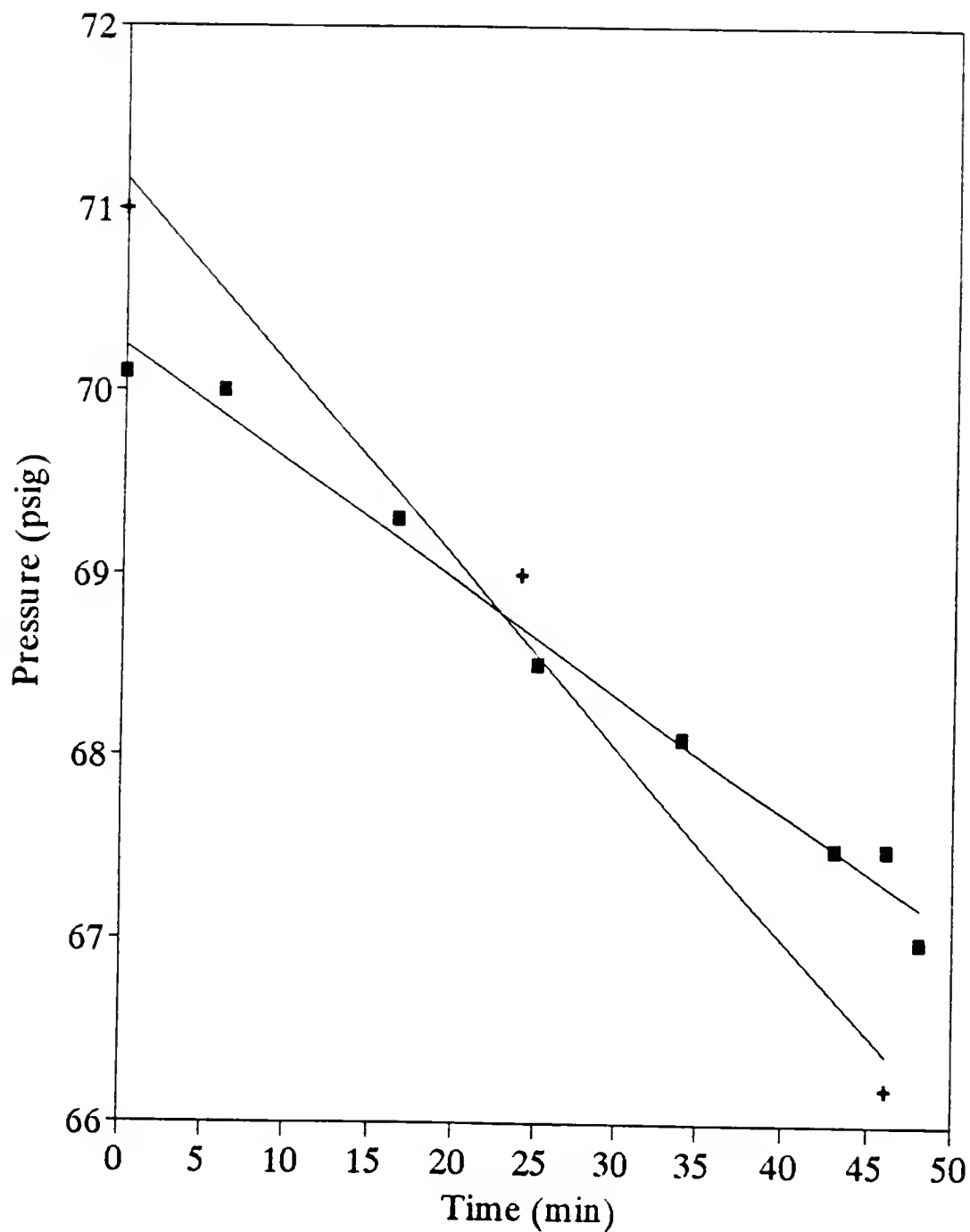Conditions: 100°C, 50 psig syn gas (1:1).

Figure 4-20. Effects of time on the hydrorformyation of 1-octene using a SHFC with a PEG 600 film. ■-Activity at the early stages of reaction. + -Activity after two hours of reaction. The degree of pore filling was 1.40 and P/Rh was 44:1.

Addition of a surfactant to the film

We wanted to test the effects that a surfactant had on the catalyst film. We chose Surfynol®485 as the surfactant because it is non-ionic and it should not interact with the active rhodium complexes. The hydroformylation of 1-octene with a catalyst that had 20% loading by mass of Surfynol®485 demonstrated an activity of 4.20 TON/min which increased to 5.42 TON/min as the reaction proceeded. The surfactant modified catalyst showed a higher initial activity at the early stages of the reaction than the standard PEG catalyst (δ for both catalysts were 1.40). The increase in activity over two hours correlates well to the highest activity attained by the PEG catalyst. This suggests that the surfactant aids in solubilizing the substrate, therefore increasing the concentration of the alkene in the film that is available for hydroformylation. The net result is increased activity. The ^{1}H and ^{31}P spectra did not have any resonances that would indicate the presence of PEG, surfactant, or phosphines in the reaction solution.

Optimized PEG system

In attempts to optimize the catalyst we studied the effects of adding water and filling the pores on the activity of the catalyst.

Variation of the film composition. While holding δ constant, the composition of the film was varied by adding water to the film. Table 4-6 and Figure 4-21 show that the activity increases as the percentage of polymer in the film increases. An

Table 4-6.   Effects of Varying Film Composition.

% PEG 600	Activity (TON/min)	n/b Ratio	# of runs
0	15.93 $\pm$ 1.62	15.6	6
25	1.18 $\pm$ 0.22	25.5	2
49	7.93 $\pm$ 0.81	5.32	2
75	16.14 $\pm$ 0.53	6.50	4
100	22.35 $\pm$ 1.74	6.02	7

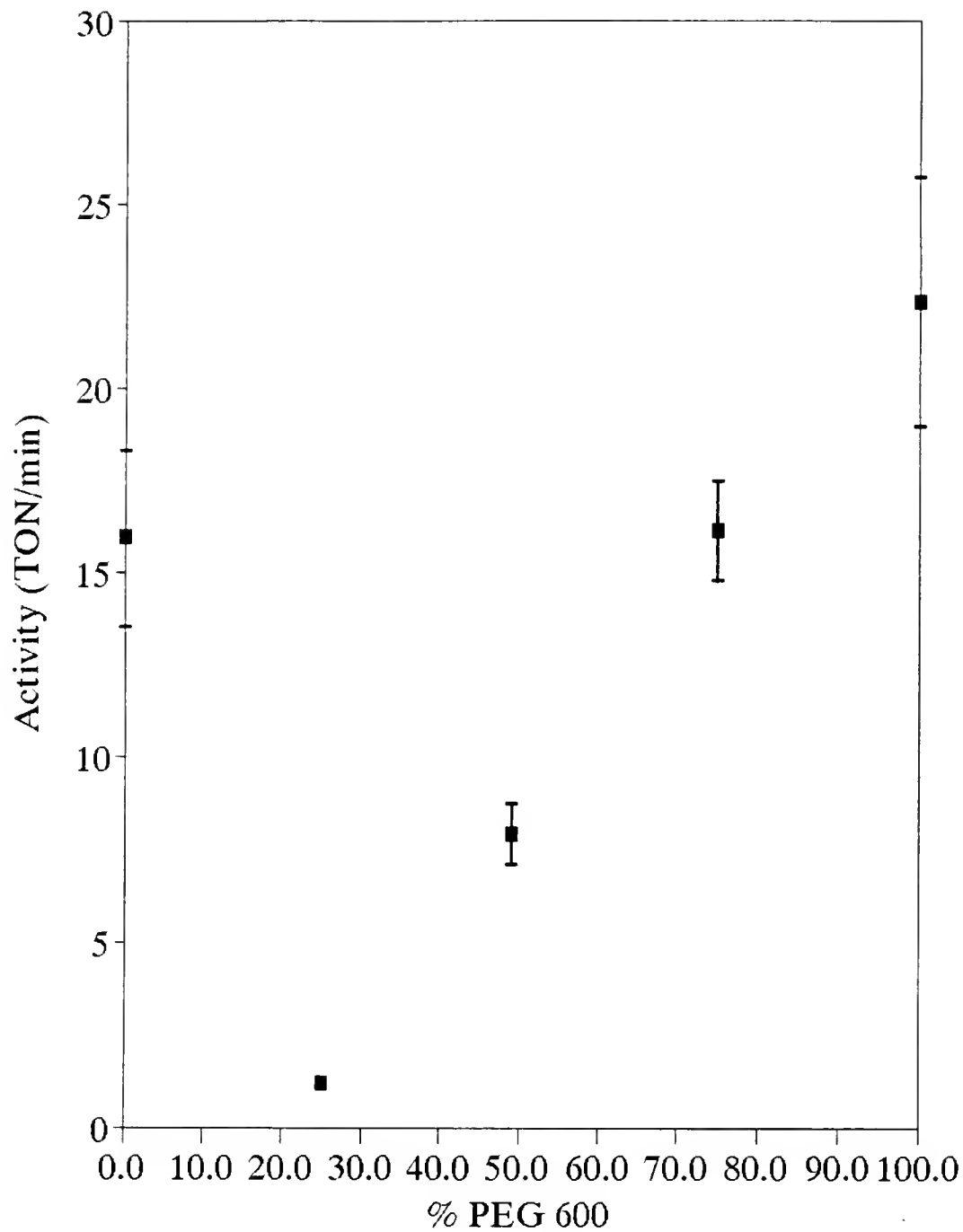Catalyst: HRh(CO)(TPPTS)$_3$/TPPTS/PEG 600/Silica gel.
Conditions: 100°C, 50 psig syn gas.

Figure 4-22. Effects of pore filling on the hydroformylation of 1-hexene.
Catalyst: HRh(CO)(TPPTS)₃/TPPTS/PEG 600/Silica gel.
Conditions: 100°C, 50 psig syn gas.
Errors calculated with Student's t distribution at F of 0.90.

interesting observation is that at 0% PEG (100% water) the activity is higher and then drops significantly with the addition of a small amount of polymer. Disturbance of the aqueous film by the polymer may explain this phenomenon.

It was noticed that water condensate formed at the top of the reactor, whenever water was used as part of the film. Horvath has stated that the aqueous film in supported aqueous phase catalysts evaporates at reaction temperatures necessary for efficient activity.[94] This evaporation leaves a rhodium complex which is bound to the support by hydrogen bonding of the hydrated sodium sulfonate groups to the support surface. Catalysts which contain solely polymers (no water) as the film phase showed no signs of condensate in the reactor.

Effects of pore volume. Davis and coworkers have reported that the degree of pore volume filled, δ, has a maximum value of approximately 0.06 with their aqueous film catalysts for the hydroformylation of 1-octene.[92] The activities of these systems are reported to drop significantly with increased pore filling. Figure 4-22 and Table 4-7 show that in the PEG systems that the activity for hydroformylation increases as the degree of pore filling increases. At 140% pore volume filled ($\delta = 1.40$) we have an extremely active catalyst (24.7 TON/min). As stated earlier this may be attributed to the development of a homogeneous system in the pores and over the surface of the support.

Table 4-7.   Effects of pore filling.

δ	Activity (TON/min)	# of runs
0.06	2.74	1
0.18	20.90 $\pm$ 2.10	3
0.50	6.85 $\pm$ 0.29	2
0.70	8.99 $\pm$ 1.74	2
1.10	11.53 $\pm$ 0.56	2
1.40	22.35 $\pm$ 1.74	7
2.00	2.96 $\pm$ 0.27	3

δ - the degree of pore filling
Catalyst: HRh(CO)(TPPTS)$_3$/TPPTS/PEG 600/Silica gel.
Conditions: 100°C, 50 psig syn gas.
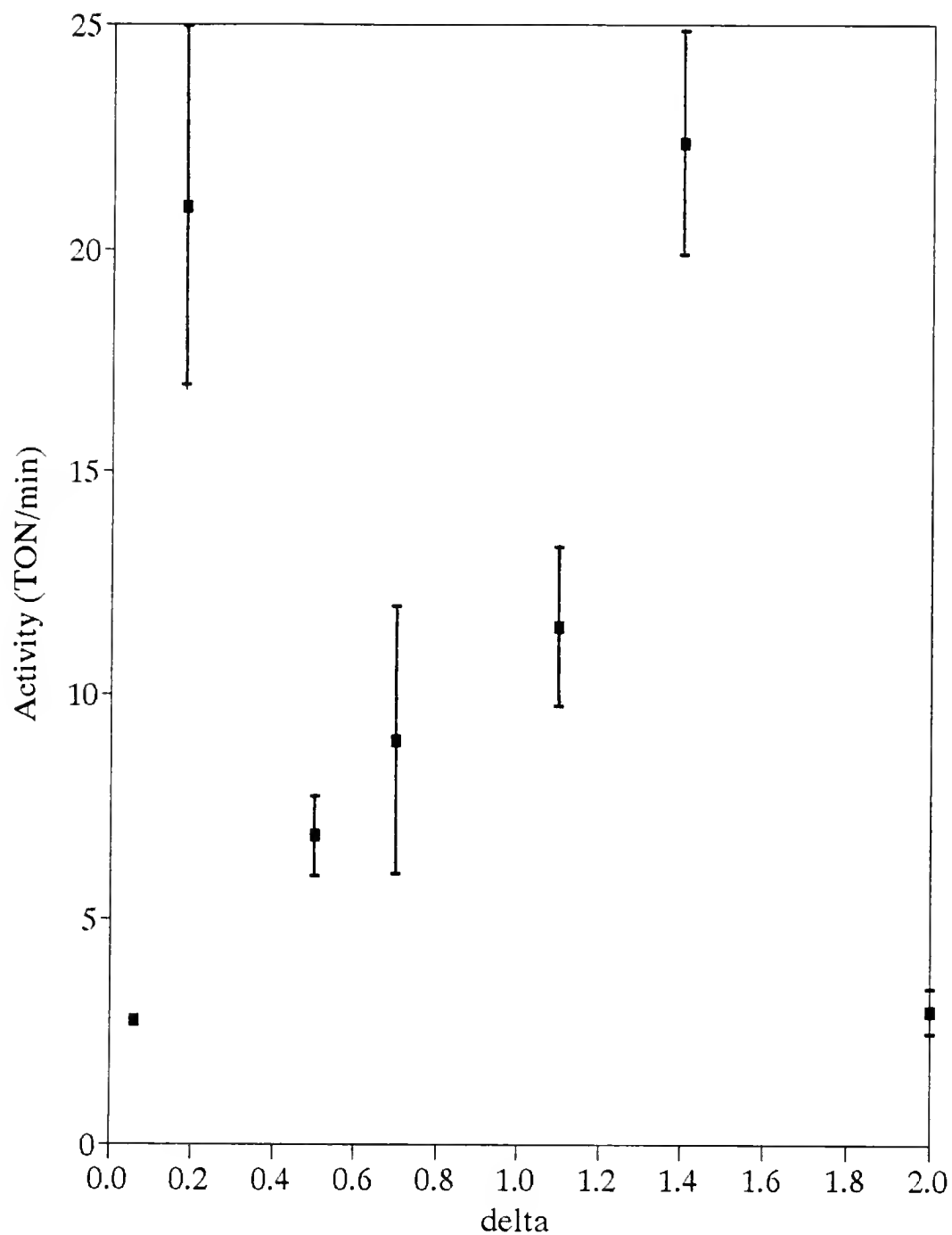
Figure 4-22. Effects of pore filling on the hydroformylation of 1-hexene.
Catalyst: HRh(CO)(TPPTS)$_3$/TPPTS/PEG 600/Silica gel.
Conditions: 100°C, 50 psig syn gas.
Errors calculated with Student's t distribution at F of 0.90.

Other films

Polymers

In addition to the low molecular weight PEG, a number of other hydrophilic polymers have been tested as catalytic films. Among these are polyethylene glycol 8000, polyvinylpyrolidinone, polyethylene oxide and polyvinyl alcohol. All are known water soluble film forming polymers.

Polyethylene glycol 8000, which is a liquid at the reaction temperature (100°C) was used to test for the effects of viscosity on the activity of the catalyst, PEG 600 has a viscosity of 10.5 gm sec^{-1} cm^{-1}while the viscosity of PEG 8000 is greater than 800 gm sec^{-1} cm^{-1}. The result was a decrease in activity from 24.7 TON/min with the PEG 600 film catalyst to 4.80 TON/min using a PEG 8000 film catalyst at 100°C. Since the change in activity was so dramatic this would suggest that the active rhodium catalyst is located within the bulk of the film. No change in activity would have suggested that most of the active rhodium sites are at the 1-hexene/polymer interface because the number of rhodium complexes at the interface should be similar in both cases. Adding water to the PEG 8000 catalyst increased the activity to 15.6 TON/min. The addition of water to this film makes the catalytic film media less viscous and more mobile. This supports the idea that the film covering the support produces a homogenous medium for the reaction. If the film is homogeneous the dispersion rhodium catalyst is uniform a less viscous liquid phase should generate a catalyst with higher activities.

Polyvinylpyrolidinone was also used as film and showed some activity but the rates were low, 0.44 TON/min. This results because PVP is solid at 100°C. This would leave only the rhodium complexes at the polymer/1-hexene interface as the only active species. Catalysts prepared with polyethylene oxide and polyvinyl alcohol were inactive toward the hydroformylation of 1-hexene (see Table 4-8).

High boiling liquids

Formamide. Besides polymers, high boiling liquids are good candidates for liquid films. Formamide is a highly polar liquid with a high degree of hydrogen bonding and is stable up to 140°C was selected as a film. A formamide film catalyst with a δ of 1.4 had an activity of 0.626 TON/min. This activity was low in comparison to the PEG 600 system mentioned previously. The selectivity was 17:1, approximately three times that of the PEG catalyst. Polar solvents are known to influence the selectivity of the catalyst for homogeneous catalysts in this manner.[11] The polar media promotes the more highly substituted rhodium phosphine complex, which is more selective toward linear products but not as active. The formamide film had appreciable volatility under the reaction conditions as evidenced by its condensation at the top of the reactor. Fourier transform infrared spectroscopy identified the condensate as formamide.

Hydroformylation with a formamide catalyst with a δ approaching zero gave an activity of 1.19 TON/min. Addition of formamide (0.5 mL) to the reaction solution lowered the activity to 0.67 TON/min but again the selectivity rose to 9.2:1.

Table 4-8.   Hydroformytlation of 1-Hexene with Various Supported Thin
Film Catalysts Using Polymers as the Film.

Film	Activity (TON/min)
Polyethylene glycol 8000	4.80
Polyethylene glycol 8000/H$_2$O	15.60
Polyethylene glycol 600	24.70
Polyvinylpyrrolidinone	0.44
Polyethylene oxide	0.00
Polyvinyl alcohol	0.00
No film	1.27

Catalyst: HRh(CO)(TPPTS)$_3$/TPPTS/Polymer/Silica
Conditions: 100°C, 50 psig syn gas.

Another aliquot of formamide gave an activity of 0.58 TON/min and the selectivity again increased to 12.4:1.

To gain the advantages of high activity in the PEG catalyst and high selectivity of the formamide catalyst a hybrid catalyst that contained both PEG and formamide in the film was prepared. A film consisting of 50% formamide and 50% PEG gave an activity of 2.81 TON/min. After two hours the activity increased to 4.26 TON/min. The selectivity, calculated as an average over time, was 9.36:1. Volatilization of formamide was again evident. Evaporation of the formamide leaves a film that is richer in PEG and this may explain the increase in the rate of hydroformylation. The ^{31}P nmr spectrum of the filtered catalyst shows the formation of both OTPPTS and HTPPTS.

Glycerol. Glycerol was chosen as another liquid phase film, namely for its insolubility in aldehydes and high boiling point (>200 °C). The activity of 1-hexene hydroformylation for this catalyst ($\delta = 1.4$) was 0.028 TON/min at 100 °C and 85 psig and an n/b ratio of 21.7. The low activity was probably due to the low solubility of the 1-hexene in the glycerol film. Again the polar nature of glycerol or the degree of solubility of the of the substrate may have contributed to the high selectivity.

Possibilities for the Active Rhodium Species

In the systems studied, the evidence indicates at least three possibilities or classes of an active rhodium species in the catalyst (see Figure 4-23).
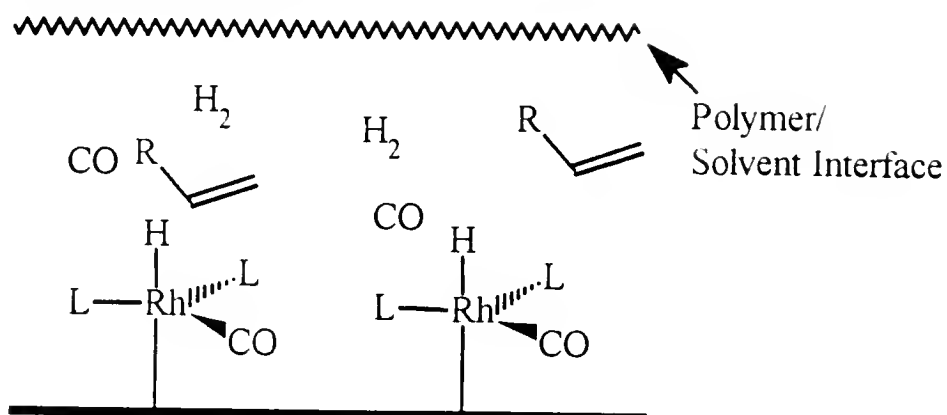
Class II. Complex at the Film/Solvent Interface
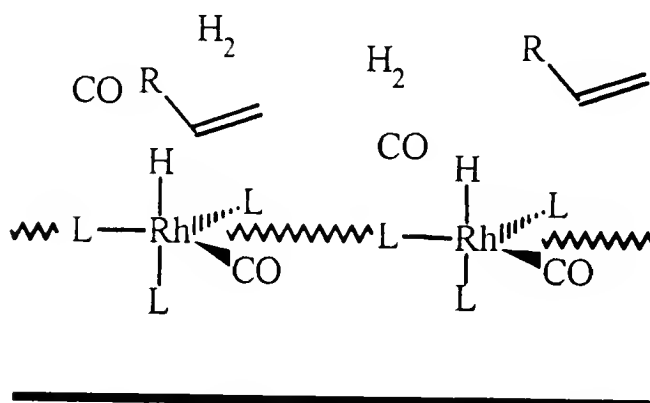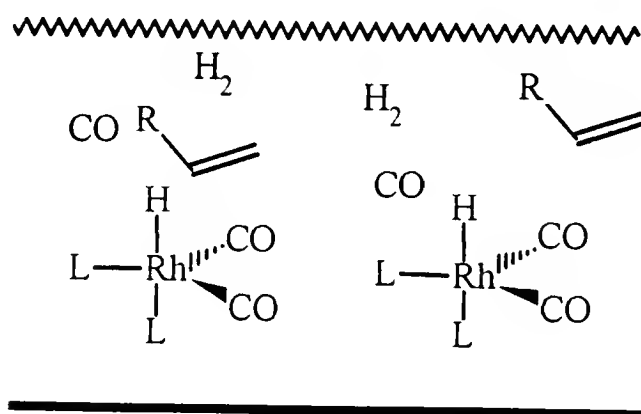

Class III. Complex in Polymer Solution

Figure 4-23. Possiblities for the environment of the active rhodium catalyst.

Class I. The first site would be a surface bound rhodium complex. This species inevitably exists but in small amounts due to the presence of the large excess of free phosphine ligand. Sulphonated triphenylphosphine will occupy most of the available surface sites that would be available for rhodium coordination. It is known that triphenylphosphine chemisorbs on silica to form the silica phosphine adduct.[33] Therefore the contribution of a surface bound rhodium species to the overall activity should be minimal.

Class II. The second site would be at the solvent/polymer interface. These rhodium complexes are probably very active but are few compared with the rhodium complex located in the bulk film. The studies of the solid hydrophilic polymers (e. g. polyvinylpyrolidinone) show that activity of the complexes at the polymer/organic interface, for a catalyst with a δ of 1.40, would be 0.40 TON/min.

Class III. The third site is located in the bulk of the polymer film. These sites are similar to homogeneous catalysts because they can be thought of as being in solution. It is evident from the viscosity and substrate studies that the activity of the supported thin film catalyst is highly dependant on the viscosity of the polymer film. The more viscous the polymer the lower the catalytic activity. If the rhodium was not in solution all of the activity would be due to rhodium at the polymer/solution interface and the activity would not vary significantly between the PEG 600 and PEG 8000 catalysts.

Conclusions

We have developed a new class of supported liquid phase catalyst which is effective for the hydroformylation of liquid substrates. Previous systems have failed because of leaching of the transition metal catalyst from the support into solution. The described system uses a water soluble catalyst $(HRh(CO)(TPPTS)_3)$ in a hydrophilic polymer covering a silica support. This catalyst relies on the polymer/organic interface to prevent leaching. We have found low molecular weight polyethylene glycol to be an effective film for this system. The hydroformylation of 1-hexene shows activities approaching 25 TON/min with n/b ratios of 6:1 and little isomerization to 2-hexene. This activity is close to that of homogeneous catalysts under the same conditions. In addition the hydroformylation of higher olefins (e. g. 1-octene and 1-octadecene) are possible. Unlike homogeneous catalysts, the catalysts described do not need an external solvent in the reaction mixture. These catalysts do not leach any of the components of the film during the initial stages of the reaction.

The polymer system has homogeneous characteristics as evidenced by nmr techniques and that the activity of the catalyst decreases with an increase in the chain length of the substrate. In addition it was found that the initial activity of the PEG 600 catalyst increases with the reaction time when 1-octene is the substrate. This suggests that some of the product aldehyde is being retained in the film and acting as a surfactant. Several polymer were used as films and it was seen that the activity

decreased with increasing viscosity and that polymers that are solids at reaction temperatures yield catalysts with low activities.

CHAPTER 5
SUMMARY

We have developed a new classification of SLPC, and have termed them supported film catalysts (SFC). These types of catalysts are a hybrid of homogeneous and heterogeneous catalytic systems. The hydroformylation of olefins were tested as a target reaction. The catalyst consists of a rhodium source, of the type $HRh(CO)(PR_3)_3$, and excess phosphine in a thin polymer film supported on silica gel. Two different systems have been developed. One system is for the hydroformylation of gaseous substrates such as propylene or 1-butene and the other system for the hydroformylation of liquid substrates.

Currently commercial processes for the hydroformylation of propylene use homogenous catalysts. While these systems are efficient, separation of costly rhodium from the reaction solution is a problem. The SFC's that we have developed use a gas flow reactor under mild conditions (50-100°C and 15-100 psig). This system produces n-butyraldehyde exclusively with conversion as high as 0.40 TON/min on a single pass. Several materials have been used as a films including rubbery polymers, such as polybutylmethacrylate, polybutadiene, silicone gum and rubber, and molten salts.

Hydroformylation of higher olefins, such as 1-hexene or 1-octene, cause new problems not seen in the gaseous system. Gas flow reactors require that both the products and reactants be gaseous and for higher olefins that requires elevated

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temperatures. The rhodium catalysts used to hydroformylate propylene deactivates at temperature greater than 120°C. The alternative is to run the reaction in the neat alkene at lower temperatures in a batch reactor. We have noticed that in a batch system the catalytic film leaches from the support. To overcome these obstacles we developed a heterogeneous catalytic system based on the water soluble catalyst $(HRh(CO)(TPPTS)_3$, $TPPTS=P(C_6H_4SO_3Na)_3)$ and phosphines in a hydrophilic polymer supported on silica gel. With these types of supported catalysts we have hydroformylated 1-hexene (25 TON/min), 1-octene (5.40 TON/min), and 1-octadecene (1.04 TON/min) under mild conditions. None of the components of the film leach into the reaction solution. The activities of the catalysts are on the order of homogeneous catalysts run under similar conditions $(HRh(CO)(PPh_3)_3$ shows an activity of 68 TON/min). This coupled with the effective hydroformylation of higher olefins (e.g. 1-octadecene) demonstrates the potential commercial application of these catalysts.

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BIOGRAPHICAL SKETCH

Michael J. Naughton was born in Rochester, New York, on January 25, 1963, to Maria Cirino and John Naughton. He graduated from Greece Athena High School in June 1981. In August 1981 he entered the State University of New York at Plattsburgh where he studied chemistry. From August 1984 to August 1985 he conducted undergraduate research under the guidance of Dr. Rudolf J. Bobka on the reactivity of ultrafine graphite. In December 1985 he graduated from SUNY Plattsburgh with a Bachelor of Science degree in chemistry.

In January 1986 he started graduate school at SUNY Plattsburgh under the direction of Dr. Edward J. Miller. He studied the synthesis of novel organometallic monomers and polymers. He graduated from SUNY Plattsburgh with a Master of Arts degree in chemistry in May 1988. In August 1987 he attended the University of Florida and joined the research group of Dr. Russell S. Drago. While working towards his degree, he studied homogeneous and heterogeneous catalysis. Upon receiving the degree of Doctor of Philosophy in inorganic chemistry, he plans to accept a NRC postdoctoral fellowship at the Army CRDEC in Aberdeen, Maryland.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.
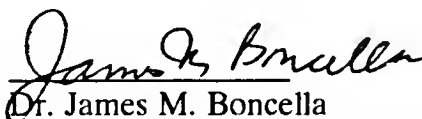
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